Catalytic Hydrocracking of Waste Plastics to Liquid Fuels

Submitted By

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Fig. 9.2 Proposed commercial process flow diagram for the hydrocracking of waste plastic.

Fig. B.1 Effect of the amount of ZC-FP catalyst in the hydrocracking of model plastic mixture for a fixed amount of 10 g plastic feed on the conversion and yields of the products. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 375°C reaction temperature.

Fig. B.2 Effect of residence time in the hydrocracking of model plastic mixture over ZC-FP catalyst on the conversion and yields of the products. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, and 20:1 feed to catalyst ratio (by weight).
Fig. B.3  Effect of initial cold hydrogen pressure in the hydrocracking of model plastic mixture over ZC-FP catalyst on the conversion and yields of the products. 500 ml autoclave reactor, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).

Fig. B.4  Effect of temperature in the hydrocracking of model plastic mixture over ZC-FP catalyst on the conversion and yields of the products. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
Abstract

The worldwide production of plastic products has been increasing rapidly over the last few decades. This increase in plastic production has resulted in gigantic amount of plastic waste. Conventional methods for waste plastic management such as landfilling and incineration are susceptible to many environmental hazards that necessitate the need of recycling of plastic wastes. Chemical recycling methods are encouraged all over the world and hydrocracking is the most advantageous process among them. Hydrocracking occurs at low temperatures and converts waste plastics into high quality liquid fuel.

In the present work, hydrocracking of a municipal waste model plastic mixture is studied using in-house synthesized mesoporous and composite catalysts. Commercial zeolite USY (CBV720), ZSM-5 (CBV2314), and beta (CP811C-300) catalysts are used to prepare their respective micro-mesoporous composite catalysts. Al-SBA-15 and various Al-SBA-16 catalysts are synthesized with increased acidic character. Some mesoporous composite catalysts with zeolite nano-seeds are also prepared. The catalysts are characterized by using SEM, TEM, XRD, EDX, N2-BET, FTIR, and py-FTIR techniques. The results of characterizations showed the desired form of the catalysts. In order to screen out some of the catalysts, hydrocracking experiments with the model plastic mixture are conducted in a high pressure autoclave reactor. Initial experiments are performed at initial cold hydrogen pressure of 20 bar, 60 min residence time, feed to catalyst ratio of 20:1 (by wt.), and at various levels of temperature (350–425°C). The products of the reactions are analyzed for conversion and yields of gas, oil (n-heptane soluble portion of liquid), and liquid. The oil produced is further analyzed with GC-FID and FTIR analysis.

On the basis of conversion and selectivity towards liquid enriched with gasoline, five best performing catalysts are chosen for additional experimentation. These catalysts are then tested with HDPE and actual waste plastic mixture. Stability of these five supports is evaluated by using spent catalysts and regenerated spent catalysts from a previous run. Two catalysts performed remarkably well in all these experiments. The two catalysts are the composite of zeolite ZSM-5 (ZC-FP) and the composite of zeolite beta (BC27). The five best catalysts are then impregnated with 0.5wt% of platinum to prepare their respective bifunctional catalysts. The performance of these five platinum impregnated catalysts is then evaluated by hydrocracking the model plastic mixture at three reaction temperatures (325°C, 350°C, and 375°C). It is found that after platinum impregnation all the catalysts produced higher conversion and higher gaseous yield than that of their corresponding catalysts without impregnation. The quality of oil obtained over these platinum catalysts is much better with higher amounts of alkanes, lower amounts of aromatics, and lower quantities of unsaturated compounds. Among these impregnated catalysts PtBC27 produced the highest liquid yield with increased gasoline content. This catalyst is then tested with actual waste plastic mixture at 60 min residence time, 20 bar initial cold hydrogen pressure, feed to catalyst ratio of 20:1 (by wt.), and reaction temperature of 375°C. It is observed that this catalyst delivered 90.1wt% conversion and 68.6wt% liquid yield with gasoline content of 65.8wt%. In parallel reactions, ZC-FP catalysts is impregnated with different combinations of metals and tested with model plastic mixture at 325°C, 350°C, and 375°C. It is found that CoRuZC-FP catalyst produced the highest liquid yield at 375°C. However, its oil contained lower quantity of gasoline than that obtained over PtZC-FP and PtPdZC-FP catalysts.

The ZC-FP catalyst is also used to investigate the effect of change in initial cold hydrogen pressure, catalyst amount, and residence time at different reaction temperatures. This data is then used to study the kinetics of the hydrocracking reaction. The regression of the experimental data is carried out and a simple kinetic model is developed where the activation energy for the hydrocracking reaction is found to be 236.8 kJ/mol. Finally, a commercial hydrocracking unit is conceptualized and a process flow diagram of the process is developed.
Declaration

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.
This work is dedicated to my mother Mubarka Munir

and

To my father Munir Ahmad Ch.
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Author
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>2D</td>
<td>Two dimensional</td>
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<tr>
<td>3D</td>
<td>Three dimensional</td>
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<tr>
<td>AIP</td>
<td>Aluminum isopropoxide</td>
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<tr>
<td>APC</td>
<td>American plastic council</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
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<tr>
<td>DCM</td>
<td>Dichloromethane</td>
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<td>DSD</td>
<td>Duales system Deutschland</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive x-ray</td>
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<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
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<td>FCC</td>
<td>Fluid catalytic cracking</td>
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<td>FID</td>
<td>Flame ionization detector</td>
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<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<td>GC</td>
<td>Gas chromatography</td>
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<td>HDPE</td>
<td>High density polyethylene</td>
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<td>LDPE</td>
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<td>MPa</td>
<td>Mega Pascal</td>
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<td>MS</td>
<td>Mass spectrometer</td>
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<td>NMR</td>
<td>Nuclear magnetic resonance spectroscopy</td>
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<tr>
<td>PBD</td>
<td>Polybutadiene</td>
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<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
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<tr>
<td>PID</td>
<td>Proportional-integral-derivative</td>
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<td>PIP</td>
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<td>PP</td>
<td>Polypropylene</td>
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<td>PVC</td>
<td>Poly vinyl chloride</td>
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<td>Py</td>
<td>Pyridine</td>
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<tr>
<td>R&amp;D</td>
<td>Research and development</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>T</td>
<td>Si or Al</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethylorthosilicate</td>
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<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<tr>
<td>TPAB</td>
<td>Tetrapropylammonium bromide</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
**List of Nomenclature**

- **B** Dimensionless activation energy
- **BJH** _d_p_ BJH adsorption average pore diameter, nm
- **BJH** _S_g_ BJH adsorption cumulative surface area of the pore between 17 Å and 3000Å width, m²/g
- **BJH** _v_p_ BJH adsorption cumulative volume of the pore between 17Å and 3000Å width, cm³/g⁻¹
- **d_p** Pore Diameter, nm
- **E_a** Activation energy, kJ/mol
- **F** Weight of plastic feed, kg
- **k** Rate constant
- **k_r** Rate constant at reference temperature
- **M** Molecular weight, kg/kmol
- **n** Order of reaction
- **N** Number of data points
- **p_o** Reference pressure, bar
- **p_{H2O}** Initial cold hydrogen pressure, bar
- **r_A** Rate of reaction
- **R** Universal gas constant, kJ/mol·K
- **S_g** Surface area, m²/g
- **S_{mi}** Micropores area, m²/g
- **t** Reaction time, min or day
- **T** Reaction temperature, °C or K
- **T_m** Melting temperature, °C or K
- **T_r** Reference temperature, °C or K
- **T_s** Softening temperature, °C or K
- **v_{mp}** Micropore volume, cm³/g
- **W** Weight of catalysts, kg
- **X** Fractional conversion of plastic feed (by weight)
- **X_{exp,i}** Experimental conversion for ith run
- **X_{mod,i}** Model conversion for ith run
- **Y_{gas}** Fractional yield of gaseous product (by weight)
- **Y_{liquid}** Fraction yield of liquid product (by weight)
- **Y_{oil}** Fractional yield of n-heptane soluble liquids, oil (by weight)
- **Y_{solid}** Fractional yield of solids (by weight)
- **ρ** Density, g/cm³
Chapter 1
Introduction

1.1 Background
The production of plastic materials such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) is increasing each year [1]. There is an increase of around 10% in plastic production from 230 million tonne in 2005 to 322 million tonne in 2015 [2]. The increase is attributed to the population increase and due to the plastic consumption in packaging, construction, agriculture, electrical and electronic appliances, health care applications, and so forth [3]. Fig. 1.1 gives an idea of this enormous production of plastics in various regions of the world [2].

![Fig. 1.1 Global quantities of the production of plastic materials in million tonne in 2015. The plastics included are only thermoplastics and polyurethanes and total production is 269 million tonne. Source of data: Ref. [2].](image)

Plastics find some unique characteristics such as outstanding versatility, light weight, firmness, resistance to water, and low cost that make them indispensable for the modern civilization [4, 5]. However, the life span of most of the plastic items is very short and most of these items have life time of less than one month [6, 7]. The huge plastic production therefore results in a gigantic plastic waste. Due to the poor biodegradability rates [7-11], the plastic waste occupies the land for a longer period of time [11, 12] as only 1-3wt% of the hydrocarbon contents of plastics are degraded in 100 years of time [11]. The plastic waste, therefore, reduces the overall landfill volume and becomes a huge environmental problem.
The landfill sites are decreasing [11, 13-17] and the cost of landfilling is soaring [16-18]. New legislations in some countries require decreased amount of waste plastics to landfill sites [7, 11]. In a landfill dump, plastic material is an environmental burden, waste of resource, source of pollutants such as stabilizers and greenhouse gases such as methane [11, 19, 20]. Incineration of these plastic wastes for getting energy results in the emission of particulate matter [19, 21, 22] and harmful gases including unburned hydrocarbons, nitrous and sulfurous oxides, and dioxins and furans [20, 23-25] that are highly unacceptable from the environmental point of view. Incineration and landfilling are therefore not the preferred routes for plastic waste management and plastic wastes are required to be treated in a more sustainable and environmentally friendly way. Recycling is an alternate method to disposal in a landfill or incineration. It not only protects the environment [26, 27] but also helps to convert the potential resource to useful products [27‒29].

1.2 Recycling of Waste Plastics

Fig. 1.2 describes the different routes of waste plastic recycling. It shows that principally the recycling of waste plastics is grouped into three methods, namely, primary or in-house recycling, secondary or mechanical recycling, and tertiary or chemical recycling.

1.2.1 Primary Recycling

Primary recycling involves the reuse of plastic products to produce the products of the same type. It involves the re-introduction of clean, single waste plastic into the extrusion assembly. It is limited type of recycling that takes place usually within the assembly line [11].

1.2.2 Secondary Recycling

Secondary or mechanical recycling involves the conversion of plastic product to produce the product of different types. This type of recycling has limited use due to the loss of plastic properties after reusing it [30, 31]. Since many years technologists have been trying to make this type of recycling successful. Efforts have been made to make the secondary product with similar mechanical properties. However, the practical experience has shown that the reprocessing of contaminated waste plastic results in the formation of polyblends that have extremely low mechanical properties and lack durability [32]. Besides that the process requires high cost for cleaning, sorting, and transporting the plastic material. Moreover, expensive additives are used during reprocessing to produce useable products [33]. The municipal waste plastic also contains many types of biological contaminates and waste plastic
is comprised of different combination of plastics. It further makes reprocessing difficult. This type of recycling is used now-a-days to make the products like boats, chairs, docks, benches, etc. However, there are serious ecological concerns about using these products [34].

This type of recycling is popular in Pakistan though it is not suitable based on the product quality, limited scope, and ecological concerns.

1.2.3 Tertiary Recycling
Tertiary recycling or chemical recycling involves the conversion of plastic waste into petrochemicals and fuels [16, 30] and thereby gaining increased attention worldwide [9, 16, 19, 23, 30, 35, 36]. Tertiary recycling is an economical and environmentally friendly way of plastic recycling and recognized as the most promising method among the various waste plastic management methods [1, 5, 37, 38]. Tertiary recycling is carried out either by a chemical or a thermal recycling technique [39]. Condensation polymers such as polyesters and polyurethanes are subjected to chemolysis (depolymerization reaction) such as glycolysis, methanolysis, hydrolysis, etc. [16, 19, 36, 40], whereas addition polymers (PE, PP, PS, and PVC) are subjected to thermal methods such as gasification, thermal cracking or pyrolysis, catalytic cracking, and hydrocracking [16, 19, 36, 41, 42].

Gasification is a process which is carried out in the presence of a reduced amount of oxygen, air, steam, etc., to produce mainly a synthesis gas, i.e., a mixture of CO and H₂. This gas is used as a substitute of natural gas and also as a feedstock in industry for the production of petrochemicals [11].

Fig. 1.2 Recycling routes for waste plastics.
Cracking is a process in which heavy polymeric molecules are broken down into smaller much lighter molecules of gaseous and liquid range. Cracking can be carried out in the presence or in the absence of hydrogen and with and without the use of a catalyst. Thermal cracking or pyrolysis is a process in which heavy polymeric molecules are broken down into smaller molecules of gaseous and liquid range using heat energy but in the absence of a catalyst. It is usually carried out at elevated temperatures and may or may not in the presence of an inert atmosphere such as nitrogen. The process of cracking requires high reaction temperature of typically more than 500°C and even up to 900°C [43]. A broad range of products is obtained in this process. The liquid product obtained as the result of pyrolysis is highly unsaturated and required to be submitted to some hydrogenation process or skeletal isomerization [44]. A lot of coke and residue is generated in this type of cracking process.

Catalytic cracking essentially requires a catalyst, usually an acidic catalyst, to carry out the process at a lower temperature and to improve the yield as well as quality of the product. In contrast to thermal cracking, catalytic cracking of polymer waste not only enhances the product selectivity but it also reduces the reaction temperature significantly. Moreover, it produces closer hydrocarbon product distribution. High quantities of hydrocarbons in gasoline range (C5-C12) are obtained as compared to thermal cracking [45, 46]. The liquids obtained contain more aromatics, more branched hydrocarbons, and less olefins [36, 47]. However, large amount of gas may be resulted due to the use of highly active catalysts in the process [48]. High deactivation rates of catalysts are observed due to which the reactor is usually designed with an adjacent regenerator and the catalyst deactivation and regeneration kinetics should be known for better operation of the process [49].

Hydrocracking is a process of cracking that requires hydrogen in the feed mixture. Due to the peculiar advantages of hydrocracking, it is discussed in rather detail in the following section.

**1.3 Hydrocracking**

Hydrocracking process is employed for the conversion of heavy (high boiling) plastic molecules to lighter (low boiling) molecules and occurs in the presence of hydrogen through carbon-carbon bond cleavage together with simultaneous or successive hydrogenation of unsaturated molecules formed during the process [50-52]. Hydrocracking is one of the most promising methods used for the conversion of waste plastics into high quality liquid fuels. It is more advantageous compared to pyrolysis and catalytic cracking as it gives highly saturated liquid product [53, 54] that is directly used, without subsequent processing, as a
transportation fuel or a fuel oil required for the energy production. Pyrolysis and catalytic cracking are considered to give unsaturated hydrocarbons [53], large amount of coke [53], and product with wide molecular weight distribution [55]. The application of hydrocracking reactions involves lower process temperatures [44] and reduced amounts of olefins [37, 43, 44, 54, 56], aromatics [43, 54], and coke formation in the reaction products. Further, the presence of hydrogen resulted in the removal of heteroatoms such as chlorine, bromine, and fluorine that may exist in a waste plastic [3, 6, 57].

Hydrocracking of a polymer generally occurs in the presence of a bifunctional catalyst in a stirred batch autoclave [58] at moderate temperatures and relatively high hydrogen pressures. Typical hydrocracking conditions are 300–450°C and 2–15 MPa cold hydrogen pressure. Heat energy is required to bring about the reaction contents to the desired temperature and to crack the long hydrocarbon chains. In the energy point of view, cracking and hydrogenation are complementary reactions as cracking is an endothermic reaction while hydrogenation is an exothermic reaction [11]. High partial pressure of hydrogen should be used in order to suppress undesirable coking or repolymerization [59]. Although non-catalytic hydrocracking (thermal hydrocracking) can possibly be realized, however, the presence of a catalyst is needed to stimulate the hydrogen addition. Catalyst used for the hydrocracking of waste plastic must have a cracking function and may have a hydrogenation-dehydrogenation function. A typical hydrocracking catalyst has an acidic support with metal impregnated over it. The acidic support is responsible for cracking and isomerization reactions whereas the hydrogenation-dehydrogenation function is performed by the metal loaded over the catalyst. In the literature, various types of acid catalysts used for the hydrotreating, cracking, and hydrocracking have been employed and studied for the hydrocracking reaction. The acidic supports that have been used commonly by the researchers for plastics hydrocracking are amorphous oxides such as silica-alumina, strong solid acids such as sulfated zirconia, crystalline zeolites such as HZSM-5 and HUSY. The metal can be a noble metal (palladium or platinum) or non-noble metal of group VI-A (molybdenum or tungsten) and group VIII-A (cobalt or nickel) of the periodic table [50].

Some of the advantages of hydrocracking over catalytic and thermal cracking are summarized below:

- Hydrocracking gives more saturated liquid product. No additional hydrogenation step is required.
- It hinders the formation of coke and prolongs the catalyst life and suggests a simple reactor system.
- This process yields high quality gasoline from a wide range of waste plastics.
- The hydrocracking reactions occur at lower process temperatures.
- It causes hydrotreating where the heteroatoms such as chlorine, bromine, and fluorine that may exist in a waste plastic are also removed.
- Cracking and hydrogenation are complementary reactions as cracking is endothermic reaction while hydrogenation is an exothermic reaction thereby saves energy.

1.4 Waste Plastics in Pakistan

Pakistan is producing 1.32 million tonne of waste plastic every year [60]. Fig 1.3 shows the plastic waste generated by different cities of Pakistan [60]. The country has the plastic waste as one of the major contributors to the solid waste. Plastic waste, especially the waste of polythene bags, is a major cause of environmental pollution, choked drains, and degradation of the sanitation network. The plastic waste is extremely harmful to the life of humans and animals due to the emission of harmful chemicals when burnt. Every year millions of birds, sea turtles, and marine animals die in the Arabian Sea alongside Pakistan due to the eating of these plastic bags [61]. Pakistan has also become a dumping ground of the plastic waste from the developed countries.

![Fig. 1.3 Plastic waste production in several cities of Pakistan. Source: Ref. [60].](image)

The waste plastic management methods in Pakistan are inadequate to cater the burden of plastic waste produced by the country. There is no systematic waste plastic management
system and the plastic waste along with the other municipal waste is dumped in landfill sites or incinerated. Both of these methods are unacceptable from environmental point of view as plastic waste emits poisonous gases and occupies the landfill sites for an extended period of time due to its slow degradation rate. There is an urgent need of non-hazardous plastic waste recycling methods to be initiated and backed by strict legislation.

Producing oil from the plastics will not only protect the environment from harmful effects of plastic accumulation or burning but it will also produce energy to meet the energy demands of the country.

1.5 Problem Statement
A series of acid catalysts is used in the literature for hydrocracking of plastics such as amorphous silica-alumina, sulfated zirconia, clays, and microporous zeolites. Out of these catalysts, microporous zeolites have shown increased activity. However, the converted products are mainly comprised of gases and resulted in rather small quantity of liquids due to the microporous cavities of the zeolites that hinder the diffusion of larger molecules. Mesoporous materials like SBA-15, SBA-16, etc., allow the diffusion of the heavy molecules and produce increased amounts of liquid products with the corresponding decreased amounts of gaseous products. The mesoporous catalysts, however, demonstrate weak acidic character and have low cracking ability compared to zeolites. Mesoporous catalysts with induced acidity and micro-mesoporous composite catalysts are therefore worth testing for the hydrocracking reaction of plastic materials.

1.6 Novelty Statement
In the present study catalytic hydrocracking of plastics is studied over various in-house synthesized catalysts. Some mesoporous catalysts with enhanced acidic character are synthesized. Along with these some composite mesoporous catalysts are also prepared with zeolite nano-seeds to take the advantage of highly acidic character of zeolites and enhanced diffusional accessibility of mesoporous materials. The work is further extended by modifying the commercially available zeolites (USY, HZSM-5, and beta) by introducing mesoporosity in their structure in order to reduce the gas yield and to enhance the conversion and liquid yield. Moreover, the catalysts are impregnated with different metals to improve the hydrogenation-dehydrogenation ability of the catalysts. A simple kinetic model is also developed and a commercial continuous process for the hydrocracking of waste plastics is conceptualized.
To my knowledge these types of catalysts have never been tested for hydrocracking of plastic materials. Moreover, kinetics of the hydrocracking of plastics in the presence of a catalyst has never been observed in the open literature. The concept of a continuous process for the hydrocracking of waste plastics has also not been found in the literature.

1.7 Thesis Objectives

Objectives of the study include:

- To synthesize acidic mesoporous catalysts, micro-mesoporous composite catalysts with zeolite nano-seeds, and modified commercial zeolite catalysts (USY, ZSM-5, and beta) with mesoporosity to obtain high conversion and increased amount of liquid product of high quality.
- To study the effect of different variables such as Si/Al ratio, TEOS/zeolite ratio, type of structure directing agent (surfactant), molarity of alkaline solution for the desilication, and hydrothermal treatment time on the properties of the catalysts finally synthesized.
- To characterize the synthesized catalysts using different characterization techniques like SEM, EDX, XRD, N₂BET, FTIR, and Py-FTIR.
- To screen out the undesired catalysts by evaluating the performance of the catalysts for hydrocracking of the model plastic mixture in an autoclave reactor. This will be achieved mainly by analyzing the conversion and quantity and quality of the liquid product at three levels of reaction temperature.
- To scrutinize further the best performing catalysts by examining their hydrocracking performance for pure high density polyethylene (HDPE) and actual waste plastic mixture.
- To evaluate the stability of the five best performing catalysts.
- To perform experiments on one of the best performing catalysts to study the effect of reaction variables such as hydrogen pressure, feed to catalyst ratio, and reaction time on the hydrocracking performance of the catalyst.
- To impregnate the five best performing catalysts with platinum metal and study the activity and selectivity of these catalysts towards the hydrocracking of the model plastic mixture.
- To impregnate various combinations of metals on one of the best performing catalysts and study the effect of these impregnations on the hydrocracking performance of the catalysts.
- To study the kinetics of catalytic hydrocracking of the model plastic mixture and develop a kinetic model by performing experiments with one of the best performing catalysts.
- To conceive a commercial hydrocracking unit employed for waste plastic conversion into liquid fuels and to develop a process flow diagram for the said hydrocracking unit.

1.8 Thesis Structure
The body of the thesis begins with an introductory chapter (Chapter 1) followed by review of the literature in Chapter 2. In this chapter a rather detailed discussion on the type of the catalysts used in the present study is provided. Special emphasis is given to the structure, properties, and applications of zeolites, mesoporous catalysts, and the micro-mesoporous composite catalysts. After this a comprehensive survey of the literature study about the hydrocracking of plastic materials is provided. The effect of different process variables and type of catalysts on the hydrocracking reaction is described in detail. Chapter 3 includes the detailed synthesis procedures of all the developed catalysts. It also includes detailed experimental setup and experimental procedure used in carrying out the hydrocracking reactions. The information regarding the product analysis and different characterization techniques is also there. Following Chapter 3, in Chapter 4, the results of the characterization for the composite micro-mesoporous USY catalysts are discussed. Also, the hydrocracking activity and selectivity performance of the USY composite catalysts are described. Chapter 5 entails the characterization of the composite micro-mesoporous ZSM-5 catalysts and outlines the results of activity and selectivity of these catalysts for the hydrocracking of the model plastic mixture. Similar to Chapter 4 and 5, Chapter 6 discusses the characterization of composite micro-mesoporous zeolite beta catalysts. It also includes the performance evaluation of the catalysts in terms of their activity and selectivity for the hydrocracking of the model plastic mixture. Chapter 7 reports the characterization, activity, and selectivity of the mesoporous catalysts and mesoporous catalysts with zeolite nano-seeds for the model plastic mixture hydrocracking. Chapter 8 is based on the five best performing catalysts discussed in the previous chapters. Additional results of the activity and selectivity of the five best catalysts for hydrocracking of HDPE and actual waste plastic mixture are presented and
discussed. The results of the stability evaluation of these catalysts are also provided. Moreover, the characterization and hydrocracking performance of the platinum impregnated catalysts is depicted. This chapter also presents the activity and selectivity evaluation of the other metal impregnated catalysts for the hydrocracking of the model plastic mixture. Chapter 9 is the last chapter and it encloses the kinetic study over one of the best performing catalysts. A simple kinetic model for the conversion and yields of gas, oil, and liquid is presented. Moreover, the process flow diagram for a commercial hydrocracking facility for the conversion of waste plastics to liquid fuels is presented. Finally, the conclusions are drawn and some future recommendations are given.

References


[34] S. Bhagat, A. Bhardawaj, P. Mittal, P. Chandak, M. Akhtar, P. Sharma, Evaluating plastic waste disposal options in Delhi using multicriteria decision analysis.


Chapter 2
Literature Review

This literature review consists of two major parts. In the first part, an introduction to zeolites consisting of their structure, synthesis, applications, and their use as a catalyst is given. This is followed by a discussion about some microporous and mesoporous materials used in the present study. In the second part of this literature review, the literature study related to the hydrocracking of a plastic material by direct liquefaction process and in the absence of a co-feed material is reviewed in detail. The effect of various operating variables is discussed and a comprehensive database of the experimental findings is developed.

2.1 Introduction to Zeolites, Mesoporous, and Micro-mesoporous Catalysts

2.1.1 Zeolites

The term zeolite is first used by a Swedish mineralogist and chemist Cronstedt who observed the discovery of naturally occurring stilbite which released significant amount of water on heating and adsorbed the water from the atmosphere when cooled [1, 2]. The use of natural zeolites is limited as their composition is not always the same and their properties are not optimized according to the catalytic reactions. On the other hand, synthetic zeolites can be produced and tailored for the desired controlled properties. Synthetic zeolites were slow to develop and use, however, a milestone was achieved in 1962 when faujasite zeolite Y was introduced in fluid catalytic cracking (FCC) for heavy petroleum distillates [3]. Today, a whole host of zeolites are extensively used in industry especially related to oil refining, petrochemical, and the synthesis of organic chemicals with kinetic diameter less than 10 Å [4]. The following reasons can be summarized for their widespread use on industrial scale [4]:

- They have high adsorption capacity and surface area
- Adsorption properties of the zeolites can be tailored according to the nature of the material
- Concentration and strength of acid sites can be modified according to the specific application
- The channel structure allows reactant, product, and transition state shape selectivity and ultimately the product distribution
- High stability of the zeolites against heat, steam, and several chemicals
2.1.1.1 Structure of Zeolites

Zeolites are crystalline aluminosilicates with highly ordered three dimensional structures. They are microporous materials and their structures consist of channels, channel intersections, and cages with dimensions of 0.2–1 nm. The SiO₄ and AlO₄⁻ tetrahedra are the basic building blocks of zeolites where the two tetrahedra share a common oxygen atom in the corner. Due to the presence of trivalent aluminum, there is a net negative charge present on each tetrahedron that has aluminum in the center. Alkali metal ions and water molecules are also present in the zeolite structure. Alkali metal cations are there to compensate the framework negative charge and thereby give rise to overall neutrality. These cations present in extra framework are ion exchangeable and result in ion exchange properties of zeolites [5, 6].

Within the framework, the quantity of aluminum can vary over a wide range, however Löwenstein formulated that the Si/Al = 1 is the lowest possible limit for zeolite framework, as the adjacent AlO₄⁻ tetrahedra are not possibly placed due to electrostatic repulsion of negative charges. Synthesis conditions determine the framework Si/Al ratio. Si or Al can also be incorporated into the zeolite framework by using post synthesis modifications. With increase in Si/Al ratio, there is an increase in hydrothermal stability and hydrophobicity and opposite is true for a decrease in Si/Al ratio.

Fig. 2.1 illustrates the structures of four selected zeolites. In these typical demonstrations, the T atoms (Si or Al) are positioned at the vertices, whereas the lines joining them stand for T–O–T linkages. Several zeolite structures arise from sodalite unit or β-cage that is formed from the linkage of 24 tetrahedra. Faujasites (zeolites X and Y) are resulted by the joining of the hexagonal faces of sodalite units by hexagonal prisms. Zeolite Y has spherical cage also known as supercage, with a diameter of 1.3 nm connected tetrahedrally. The pore structure of ZSM-12 is unidimensional 12-membered ring. Pentasil unit is the building block of ZSM-5 and its all-silica form is silicalite-1. It consists of 10-membered ring pore structure, having intersecting system, one of them straight and the other one sinusoidal [3].

Fig. 2.2 shows the pore structure of typical porous solids, it shows how molecular size of some chemical compounds falls within the range of zeolite pore sizes. This property is especially beneficial in shape selectivity of zeolites to be discussed later.
2.1.1.2 Synthesis of Zeolites

For the synthesis of zeolites a wide range of experimental conditions is used. Typically, these materials are synthesized using hydrothermal treatment in a teflon-lined stainless steel autoclave. Temperature conditions vary from 120–300°C under autogenous pressure. Reaction mixture is composed typically of a silica compound, alumina compound, water, and a suitable surfactant. An alkaline medium (NaOH) is used for microporous zeolite synthesis. Some of the important preparation parameters are discussed below:

Reaction mixture composition: The composition of the reaction mixture, i.e., the ratios of different components is an important factor in determining the quality of zeolite produced. For instance an increase in the base concentration results in the retention of higher silicate concentration in the solution which results in the formation of zeolite with lower Si/Al ratio [7].

Agitation: Agitation is usually preferred during synthesis as it maintains the temperature homogeneity. However, agitation is not recommended in some cases. Some zeolites are synthesized in static condition, whereas the others crystallize under stirring. High degree of supersaturation inside the small pores of the gel particles may be decreased by the movement
of liquid phase that may inhibit the process of nucleation of the metastable phase inside the small pores [7].

Fig. 2.2 Pore diameter distribution of typical porous solids. KA shows the K form of zeolite A and VPI-5 represents microporous aluminophosphate having 18-membered ring pores. For comparison, the kinetic diameters of methane, water and neopentane are also indicated. Source: Ref. [3].

Reaction time: The reaction time for the crystallization varies from several hours to several days. The reaction time varies with the type of reaction mixture as well as the type of material used. The reaction temperature may also decide the reaction time. Lower temperature may need more time as compared to higher temperature.

Crystallization temperature: Temperatures used to synthesize zeolitic materials range from room temperature to 350°C. Rates of reaction and crystallization increase with an increase in reaction temperature. At lower temperature with water as template a somewhat open zeolite may be obtained [7].

Presence of templates: Different types of surface directing agents or templates are used for the synthesis process. The inorganic templates used are anions and/or cations of bases (e.g., LiOH and NaOH), acids (e.g., HF), or salts (e.g., NH₄F and NaCl) that are added as such in
those cases where they do not exist previously as a source of T element. Organic templates are also used and they are selected from a large variety of alkyl- or arylammonium hydroxides or amines, salts, alcohols, etc. [7].

Other variables: Other variables such as ageing, pressure, order of addition of reactant materials, nature of mixing, and amount of salts are also important as they also affect the synthesis of zeolites. Moreover, source of energy such as microwave (energy) synthesis can also substitute the conventional hydrothermal synthesis.

2.1.1.3 Applications of Zeolites

Primarily zeolites are used for three applications, i.e., catalysis, adsorption, and ion exchange. Due to the low cost of natural zeolites they are used in bulk mineral applications.

Zeolites as adsorbents: Typical adsorbent applications of zeolites include bulk separations, working on molecular sieving principle, and elimination of small polar molecules by more aluminum containing zeolites. Zeolites are used for drying of natural gas and cracking gas, for CO₂ removal from natural gases and flue gases, and for pollution abatement by removing Hg, NOₓ, and SOₓ. Zeolites molecular sieves are also used for the bulk separation of n- and iso-paraffins, p-xylene, olefins, oxygen from air, and fructose from mixed sugar solutions [8].

Zeolites as catalysts: Heterogeneous catalysis is the most important area of zeolites application. Zeolites are used as a catalyst in inorganic reactions like NO reduction to NH₃ and oxidation of H₂S. They are also used in a variety of organic reactions like aromatization of hydrocarbons, alkylation, chloroaromatics dechlorination, chlorocarbon oxidationg, etc. [9–14]. Moreover, zeolites are successfully used for hydrocarbon conversion reactions like cracking, hydrocracking, and isomerization. These materials are also frequently used in industry for Friedel-Craft reaction of aromatic compounds, methanation, and shape-selective reforming [15, 16].

Zeolites in ion-exchange applications: Zeolites are used in many ion exchange applications. These materials are used in detergents for softening the water as well to reduce the hardness of water to be used in industrial boilers and heat exchangers. In these applications, Zeolite A selectively removes Ca²⁺ and replaces it with less undesirable sodium ion. Zeolites also find their applications in the removal of undesired radioisotopes from radioactive wastes. These
materials are also used for the removal of NH$_4^+$ from wastewater and removal and recovery of metals [15].

2.1.1.4 Zeolite Functionalization as a Catalyst

Many hydrocarbon reactions are supported by acidic catalysts. Zeolites that are ion exchanged by NH$_4^+$, heated, and undergone steaming operation can acquire strong acidic sites that are useful in reactions like cracking and isomerization. Classical Brønsted and Lewis acid models are used to classify the acid sites of zeolites. Proton donor acidity corresponds to Brønsted acidity, whereas Lewis acidity corresponds to electron pair acceptors. When the negatively charged framework is balanced by the protons (H$^+$), then Brønsted acidity occurs. Lewis acid site are perceived by the trigonally coordinated aluminum atom possessing a vacant orbital that can accept an electron pair. To create Brønsted acidic sites in synthesized zeolites the extraframework cations are exchanged for NH$_4^+$ cations, then the NH$_4^+$ exchanged material is calcined, leaves protons as the charge balancing extraframework cation. These protons are highly acidic and involved in bridging hydroxyl groups, rendering the resultant materials extremely effective as solid acid catalysts of oil refining and petrochemicals industry.

Zeolites are capable of acquiring high concentration of reactants inside their cages and channels, greater than gas phase concentration. This high concentration supports bimolecular reactions of hydrogen transfer. Moreover, siliceous zeolites are not hydrophilic but organophilic in nature. The organophilic character of zeolites is required to convert oxygenated hydrocarbon compounds to paraffinic and aromatic hydrocarbons. Alkali or alkaline metal atoms present in zeolites are capable of being ion exchanged. This property is used to give diverse catalytic properties to the zeolites. With their pore sizes in the range of molecular dimensions, zeolites behave like molecular sieving and together with catalytic properties they are shape selective catalysts. Another unique characteristic of zeolites is the high accessibility of internal surfaces and it constitutes more than 98% of the total surface area. Typically, the surface areas are of the order of 300–700 m$^2$/g [5]. Greater surface area is directly related to greater accessibility of acid sites.

*Isomeric substitution*: Isomeric substitution is a method to replace an atom in a crystal structure by another atom that has similar cation radius and valence number. It is a useful method to introduce a moderate amount of active centers into the structure of a zeolite. Isomeric substitution can either be introduced during the zeolite synthesis or in the post
synthesis modification. The formation of the titanosilicalite, TS-1, is an example of isomorphic substitution [17]. Titanium cations are introduced in all-silica zeolites. At random sites in MFI framework, titanium cations are substituted for silicon centers, introducing oxidation-reduction functionality to the catalyst and developing a novel selective oxidation catalyst [18, 19].

*Cation exchange:* The aluminum presence in the framework of zeolites gives these materials a net negative charge. That negative charge is electrostatically balanced by extra-framework cations that may be comparatively mobile. These cations can easily be exchanged with other cations depending on the type of zeolite. Si/Al ratio plays a significant role and it determines the cation concentration, placement, and exchange selectivity. It is an important factor in catalysis, adsorption, and ion-exchange applications. However, there is decrease in acid site concentration with increase in Si/Al ratio whereas with a decrease in aluminum content the acid strength and proton activity coefficients are increased. Cu, Co, Pt, Pd, etc., are mostly used for cation exchange of zeolites. Typical ion exchange of a zeolite involves stirring of the zeolite in an aqueous solution of a soluble salt containing the desired cation at a certain temperature [20].

*Shape selective catalysis:* Shape selective catalysis is one of the most important characteristics of zeolites. The narrow pore structure of zeolites is responsible for the shape selective behavior and it strongly influences the final product distribution. Shape selectivity can be divided into the following three types:

- Reactant shape selectivity as illustrated in Fig. 2.3a shows the way of approach of straight chain hydrocarbons into the pore and can therefore react, but branched chains are not able to enter. Molecules with dimensions smaller than a critical size can enter the pores only, reach the catalytic sites, and react there.
- Product shape selectivity as shown in Fig. 2.3b demonstrates that a mixture of all three isomers of xylene is formed in the cavities but only the para form is able to escape. The product below a specific kinetic diameter can only leave the active sites and diffuses out through the channels.
- Transition state shape selectivity as shown in Fig. 2.3c demonstrates the transalkylation of dialkylbenzenes. This kind of shape selectivity can restrain or check the formation of intermediates in a reaction. The reactions that require the smallest transition state will
move ahead unchecked. It is therefore important to say that a reaction is limited more by its mechanism than by diffusion limitations [18, 22].

2.1.1.5 Some Important Zeolites

Zeolite USY: Zeolite Y is modified to produce ultrastable Y zeolite (USY). The modification is performed at high temperature by steam treatment and it is necessary as the structure of unmodified zeolite Y collapses during the process of regeneration. USY has, therefore, structure that is more thermally stable than that of zeolite Y. Y zeolites are faujasites that consist of several tertiary building blocks known as sodalite cages (Fig. 2.1). These sodalite units are joined by their hexagonal faces through hexagonal prisms to form a supercage or α-cage.
Zeolite Y has a pore size of 0.74 nm, however, the dimension of the supercage (a cavity inside the pores) formed is 1.2 nm. The pore structure is wide enough to allow the relatively bigger reactant molecules to enter into the supercage. However, still larger molecules are prohibited and zeolite Y offers the catalyst shape selectivity as it allows only selective molecules to enter through the pore openings into the supercage. Both Bronsted acidity and Lewis acidity are involved in cracking activity of these materials. During hydrothermal treatment, there is a change in the structure of zeolites Y where some aluminum ions, from the framework, are extracted out and result in the formation of new Lewis acid sites. However, the ion exchange capacity is decreased during this modification. The extent of increase in the catalytic activity depends on the concentration of Al framework ions in zeolite Y and also on the intensity of steaming process. Acidic form of USY is used to increase the gasoline and diesel yield from the catalytic cracking of crude oil in petroleum refineries. USY zeolite supported platinum/palladium metal catalyst may be employed in the hydrocracking and hydroisomerization of relevant refinery fractions [17, 19, 23].

Zeolite ZSM-5: Zeolite ZSM-5 is named from Zeolite Socony Mobil No. 5, and frequently used in its hydrogen form (H-ZSM-5). Zeolite ZSM-5 is made of pentasil units and comprised of intersecting systems of ten-membered ring pores, one is zig-zag and the other is straight (Fig. 2.1). Straight channels are parallel to b axis, through elliptical openings of 0.51 × 0.55 nm, intersect zig-zag channels with nearly circular 0.53 × 0.56 nm apertures. No channel exists in c direction. ZSM-5 is an important industrial catalyst in heterogeneous catalysis. The zeolite ZSM-5 is considered as a model shape selective catalyst [3, 19] and can be synthesized with a silica/aluminum ratio of 5–8000 and its structure is not varied greatly by this change in ratio. With increase in Si/Al ratio, thermal, hydrothermal, and acid stability increase. As acid strength and the number of acid sites depend on the number of aluminum atoms present, there is an increase in the strength of zeolite's acidity with decrease in Si/Al ratio and therefore comparable to concentrated sulfuric acid [24]. The pore size of ZSM-5 is approximately 0.52 to 0.58 nm, and therefore it has small coking tendency. It is used in the isomerization of xylenes, disproportionation of toluene, and in the synthesis of ethylbenzene. It is also used for the enhancement of octane number and olefin content in FCC gasoline yields [25].

Zeolite beta: Zeolite beta has small crystal size of about 20–50 nm. Unlike zeolite ZSM-5, it can be prepared with lower Si/Al ratios of 10–100. Zeolite beta has a complex structure. It is
comprised of three interconnecting pore systems, having two (Polymorph A and Polymorph B) 12-membered ring channels (0.57 × 0.75nm) in diverse crystallographic directions intersect partly, while a third zig-zag channel (0.56 × 0.65nm) is formed by these intersections (Fig. 2.4). The diameter of cavities is 0.76 nm showing that the three-dimensional structure of zeolite beta has no cavities or supercage. It is, therefore, categorized as a large pore zeolite between Y zeolite and mordenite. Since reduced diffusion limitations are encountered, zeolite beta is considered valuable in the reactions that involve the synthesis of bulky molecules. Furthermore, it is of great industrial importance due to its specific pore system and highly acidic nature. This catalyst is therefore considered good for many important reactions like dewaxing, hydrotreating, cracking, benzene alkylation with light olefins, isopropylation of cumene to diisopropylbenzene, and isobutane alkylation with n-butene [26‒29].

![Fig. 2.4 Structure of zeolite beta: a) Polymorph A, b) Polymorph B. Source: Ref. [30]](image)

### 2.1.1.6 Limitations of Zeolites

In spite of the catalytically desired characteristics of zeolites they become rather inefficient when dealing with the large sized molecules, i.e., larger than the pore size of the zeolites. In these processes the need of using a mesoporous zeolite, having sufficient pore dimension to cater larger molecules, evolves [4].

Applications of zeolites are limited due to their relatively small pore openings. They can convert molecules having kinetic diameters below 1 nm. However, the use of zeolites is restricted when the molecular dimensions of reactants are greater than this. Therefore, for the heavy oil cracking, a persistent demand has been developed for well-defined large size pore structures. Mesoporous silica is considered an ideal solid support owing to its tunable pore size, high surface area, presence of the hydroxyl groups on the pore walls, and presence of large number of highly dispersed active sites [31]. The mesoporous cavities provide easy
access to heavy molecules that have diffusion limitation with small microporous cavities and these materials have good catalytic activity as well [4, 32].

2.1.2 Mesoporous Aluminosilicate/Silicate Materials

Mobil Corporation scientists in 1992 discovered the M41S family of aluminosilicate/silicate mesoporous materials. This paved the way for the new class of materials different to that of microporous zeolitic materials. The mesoporous materials (pore size 2 and 50 nm) are ordered or disordered materials and found to have exceptionally large pore dimensions and possess extremely high surface area >1000 m²/g. The pore size of these materials allows large molecules to reach the active sites present within the pore channels with reduced diffusional resistance. The regular pore dimensions and the extended surface area provide an opportunity for these materials to become an excellent catalyst support. However, the mesoporous structures generally have weak hydrothermal stability and reduced or no acidity required for many industrially important reactions. Their structure can be improved and the acidity can be introduced as desired. Mesoporous materials are formed in the presence of a long chain organic template and acid or basic atmosphere. The diameters of these mesopores can be tailored to the desired value (1.8–10 nm) by the proper choice of the synthesis methods.

Many different types of mesoporous structures have now been synthesized and have widely been used in catalysis, separation, and as sensing elements. Examples are MCM-41, SBA-15, and SBA-16.

2.1.2.1 Some Important Mesoporous Materials

MCM-41: MCM-41 has gained attention owing to its high specific surface area, controlled pore size, hydrophobicity, and acidity. It is comprised of hexagonally arranged unidimensional pores, the size of which can be varied within 2–10 nm depending on the preparation methods and the conditions. The MCM-41 materials are prepared conventionally by hydrothermal treatment. Their structures are found to be made of amorphous inorganic silica walls around surfactant molecules. The pore size of MCM-41 molecular sieve is extensively uniform, as compared to the other mesoporous materials such as intercalated clays. The pore size uniformity is comparable to that of zeolites, however, the silica or the silica-alumina pore walls are non-crystalline contrary to zeolites [3].

SBA-15: SBA-15 is first reported by Zhoa et al. [33, 34]. It is a 2D ordered hexagonal mesostructure with (space group p6mm) uniform pore size distribution. These materials have the pore diameters from ~6.5 to 10 nm. The pore wall thickness of these materials lies in the
range of 3.1–4.8 nm which is much greater as compared to MCM-41. As a result, these materials have higher hydrothermal and thermal stability [33–35]. As evident from NMR analysis, the silica is also inserted into the framework by the organic template [36]. The mesopores that are generated after the removal of template by calcination, linked with the micropores or small mesopores. However, these micropores (pore sizes from 1–3 nm) are arranged disorderly, therefore no diffraction peak is attributed to these micropores in XRD patterns [37, 38]. About 30% of total volume is contributed by the intraframework pore volume [39]. Addition of a small amount of a co-solvent like ethanol or a salt in the synthesis mixture may help to control the microporosity in SBA-15 [37]. Acidity of the SBA-15 catalysts also significantly increases by the addition of aluminum into the mesostructure.

**SBA-16:** SBA-16 is first described by Stucky [33, 34] and his co-workers in 1998. It is a mesoporous material having 3D cubic structure and belongs to Im3m space group [40]. Images of electron microscopy illustrate that each mesopore in the body-centered cubic array is connected with its eight neighbors [41]. This offers more promising mass transfer than in the unidirectional pore system of other hexagonal mesoporous materials such as SBA-15 [42]. The family of SBA has greater pore diameter and thicker pore walls that results in higher thermal stability as compared to MCM family. Furthermore, the templates used for the synthesis of these materials are nontoxic, biodegradable, and cheap [33, 34]. The interesting structure of SBA-16 makes it an attractive material for catalysis. However, due to its difficult synthesis procedure it is not widely studied [43]. The insertion of aluminum into silicious SBA-16 mesostructure results in the increase of acidic character of the catalyst. There is, but, a problem of aluminum insertion into these structures. The synthesis of these materials needs less than 1.0 pH, however at this pH the aluminum ions are cationic aquo-species rather than oxo-species that is needed for effective aluminum insertion into the framework of mesostructure [44].

### 2.1.3 Micro-mesoporous Composites

As mentioned before, in spite of the catalytically desired characteristics of zeolites, they turn out to be insufficient when the reactant molecules are larger than their pore dimensions. On the other hand, despite of the remarkable advancement made in producing the mesostructures, the catalysts synthesized so far are not that active as well as stable as required for the modern catalytic processes. In other words, the mesoporous catalysts exhibit weak acidic character and low hydrothermal stability as compared to zeolites. These features restrict the use of
mesoporous catalysts in many industrial reactions. Therefore, for the processing of large molecules such as vacuum gas oils that need to be cracked and hydrocracked, another approach is gaining attention now a days. It involves the combination of mesopores and micropores together with the stability of microporous zeolites. In these micro-mesoporous composites, the advantage of pore structure of zeolites is obtained along with the presence of desired mesopores.

Many researchers have been working from the past few years to develop the micro-mesoporous composite catalysts. A number of different approaches can be used for the synthesis of these materials. They can be prepared first by the preparation of mesoporous material and then partial transformation of some of its structure into microporous phase. These materials can also be prepared by the preparation of zeolite precursor first and then generation of mesoporous phase by the accumulation of surfactant of mesoporous materials with the zeolite precursor [45‒49] as shown in Fig. 2.5. Ooi et al. [49] used this method for the preparation of composite zeolite beta/MCM-41. This catalyst showed excellent cracking activity for palm oil. Another method involves the hydrothermal treatment of the mixture of microporous and mesoporous precursors that are prepared simultaneously [50, 51]. There are some other popular methods to generate mesopores in microporous zeolites like dealumination or desilication of already synthesized zeolites using acids or alkalis and then adding the template of mesoporous materials for generating the mesopores at the defective sites created by the removal of silica or aluminum from the framework of zeolites [52‒56].

![Fig. 2.5 An illustrative example of the preparation of micro-mesoporous composite material. Source: Ref. [57].](image)

The use of carbon materials (particles of carbon black, carbon aerogel, colloid-imprinted carbon) as hard template for the synthesis of microporous structure [58‒60] is also practiced. In this method mesoporous phase is generated after the removal of carbon particles. Micro-mesoporous composite zeolites can also be prepared by the assembly of zeolite hydrolysis
products. By using this approach alkali treated MOR zeolite is assembled into hydrothermally stable MOR/MCM-41 [61]. This technique is also used to prepare highly acidic and active mesoporous ZSM-5 that is synthesized by the assembly of hydrolysis product of ZSM-5 [62]. Zeolite faujasite (FAU) coated with a thin layer of mesoporous MCM-41 was first reported by Kloetstra et al. [63]. They studied the micro-mesoporous composite zeolite synthesis by the preparation of zeolite faujasite (FAU) first and then coating it with a thin layer of mesoporous material. Karlsson and co-workers [64] used the two templates gel system for the in-situ preparation of MFI zeolite and MCM-41 for making micro-mesoporous composites. Huang et al. [65] attempted the composite of MCM-41/ZSM-5 by using dual surface active agents technique through two-step crystallization. The structure resulted have interconnected microporous and mesoporous framework. Guo et al [66, 67] used the same method for the preparation of MCM-41/Beta. Xiao and co-workers [68, 69] used co-templates (tetraethylammonium hydroxide and cetyltrimethylammonium bromide) for the preparation of thermally stable and highly acidic composite catalysts. Highly acidic and ultrastable mesoporous aluminosilicates with zeolite gel are also reported by Kaliaguine and co-workers [70, 71]. Cubic hollow structured mesoporous aluminosilicates having zeolite seeds have also been synthesized using a one-step method [72, 73]. However, most of the researchers used one dimensional mesoporous structures like SBA-15 and MCM-41 in micro-mesoporous composites [50, 63–67]. This could be attributed to difficult synthesis of cubic phase like MCM-48 and SBA-16. However, Bein and co-workers [50] synthesized the composite of zeolite beta and MCM-48 by treating simultaneously the mixture of MCM-48 precursor at high temperature and X-ray treated amorphous seeds of zeolites. Xia and Mokaya [74] reported the composite of ZSM-5/MCM-48 by using two-step crystallization technique.

2.2 Hydrocracking of Plastic Materials using Direct Liquefaction Process

Hydrocracking of virgin and waste plastics using direct liquefaction process without the addition of a co-feed has been studied by a wide range of investigators. A part of these researchers studied the hydrocracking of a single type of plastic material while the others studied mixture of these individual plastics. The hydrocracking reactions were studied both in the presence and absence of a catalyst and the effects of various operating parameters such as temperature, hydrogen pressure, reaction time, catalyst type, and catalyst loading were studied. Generally, the hydrocracking reactions were carried out in a closed tubing bomb (shaking type) reactor or batch stirred autoclave where the feed and catalyst were charged initially and hydrogen pressure was set in cold conditions. The products of the reaction were
analyzed for gas yield, oil yield, i.e., lower molecular weight liquid fraction obtained by extraction using n-pentane, n-hexane, etc., total liquid yield that included pre-asphaltenes and asphaltenes and obtained usually by tetrahydrofuran (THF) extraction, and solid residue. In a few studies, unreacted polymer and coke content were also measured. GC-MS and GC-FID were used to identify and quantify the product components and simulated distillation was carried out to develop a relationship between the boiling point temperature and the percent distilled which was later used to evaluate the yields of low boiling and high boiling fractions of the oil obtained. Table 2.1 shows the list of the investigators along with the reaction conditions, catalysts, and analysis techniques employed by the investigators whereas Table A-1 in Appendix A is an extensive database of their experimental findings. The tables include only those studies that involve the direct liquefaction of a plastic material by hydrocracking reaction without the addition of any solvent, waste oil, heavy oil, coal, biomass, etc. In the sections to follow, the ratios and percent values such as catalyst loadings and yields are reported by weight and hydrogen pressures are at cold conditions unless clearly stated.

2.2.1 Effect of Reaction Parameters on Hydrocracking of Plastic Materials

2.2.1.1 Effect of Catalyst on Plastic Hydrocracking

Catalysts play a key role in plastic hydrocracking. As discussed earlier, a bifunctional catalyst is usually required for this purpose. The presence of acidic function as well as hydrogenation-dehydrogenation function is normally required for achieving appreciable conversion, high yield and superior quality of liquid products, and reduced amount of coke deposits. A metal supported solid acid such as sulfated zirconia or zeolite is a good choice for this type of reaction. A suitable catalyst yields a liquid product that has lower boiling point with greater iso- to n-alkane ratio and that has a lower bromine number (reduced amount of olefins). Different types of commercially available and development catalysts designed for cracking, hydrocracking, and hydrotreating processes are used in the literature to observe their effectiveness towards the hydrocracking of a plastic material.

Venkatesh et al. [75] employed ZrO$_2$/SO$_4$, 0.5%Pt/ZrO$_2$/SO$_4$, 2.0%Ni/ZrO$_2$/SO$_4$, and 1.0%Pt/$\gamma$-Al$_2$O$_3$ catalysts for the hydrocracking of HDPE (high density polyethylene), PP, and PS. No experiment was performed in non-catalytic conditions for the comparison. For the hydrocracking reaction of HDPE at 375°C and 8.38 MPa H$_2$ pressure (reaction time of 25 min and feed to catalyst ratio of 5:1) over 0.5%Pt/ZrO$_2$/SO$_4$ and 2.0%Ni/ZrO$_2$/SO$_4$ virtually same conversion was obtained on each catalyst. In both the cases, high iso- to n-alkane ratios were obtained, however, with Ni-loaded sulfated zirconia catalyst the ratio was slightly better
in C4–C9 range. It was proposed by the authors that the higher amounts of isomers obtained with Ni metal were due to the lower hydrogenation-dehydrogenation activity of Ni metal giving lower concentration of hydride ions on the surface of the catalyst due to which the carbenium ions formed on the catalyst surface underwent considerable isomerization before being desorbed by hydride transfer.

For both the above catalysts, PP was degraded completely at 325°C MPa, however, with no metal function, i.e., over ZrO2/SO4 and with weak acidic function, i.e., over 1.0%Pt/γ-Al2O3 catalyst, the cracking of PP was not realized and in both the cases insignificant conversions were obtained. These results suggest the use of a bifunctional catalyst, as expected for a hydrocracking reaction, with strong acidic function and a hydrogenation-dehydrogenation function for the hydrocracking of plastic materials especially for the conversions at lower temperatures. It is important to mention here that Venkatesh et al. [75] suspected the stability of sulfated zirconia catalysts as they observed a significant loss in sulfur during the hydrocracking reaction which is responsible, in the form of SO4^2- (sulfate ions), for the activity of the catalyst. In another study by Venkatesh et al. [76] hydrocracking of HDPE was reported on two different Pt-loaded zirconia supports. Under the conditions of 375°C, 8.38 MPa H2 pressure, 25 min residence time, and 5:1 feed to catalyst ratio, nearly same conversion was obtained over both 0.5%Pt/ZrO2/SO4 and 0.5%Pt/ZrO2/WO3 catalysts. Higher liquid yield and lesser amount of gases with lower iso- to n-alkane ratios were obtained with 0.5%Pt/ZrO2/WO3. Venkatesh et al. [76] explained the decreased amount of gases produced on the basis of lesser acidic activity of the 0.5%Pt/ZrO2/WO3 catalyst. However, the ratio of iso- to n-alkane in the reaction product is generally not only a function of support acidity but it also depends upon the relative strength of metal and acidic functions [77]. With PP at 325°C, 8.38 MPa H2 pressure, 60 min reaction time, and 5:1 feed to catalyst ratio, almost 100% conversion was obtained over both the catalysts with very high yields of gases. Again, 0.5%Pt/ZrO2/SO4 catalyst was found more selective towards gases. These high gas yields over the catalysts were caused possibly due to the presence of a large amount of catalyst in the reaction mixture [78] and increased residence time. Although 0.5%Pt/ZrO2/SO4 catalyst was found slightly more active but 0.5%Pt/ZrO2/WO3 catalyst was found more stable as no loss in tungstate ions was observed.
Table 2.1 List of research works carried out on direct liquefaction of plastic material by hydrocracking

<table>
<thead>
<tr>
<th>Researcher/s (year)</th>
<th>Feed</th>
<th>Catalyst</th>
<th>Reactor</th>
<th>Condition</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmer et al. (1995) [105]</td>
<td>PE, PP</td>
<td>No catalyst</td>
<td>15 cm³ SS (batch, tubing bomb, shaking type)</td>
<td>( F = 2.0 ) g, ( t = 5–60 ) min, ( p_{\text{H}_2,O} = 3.55 ) MPa, ( T = 425–525°C )</td>
<td>Conversion: THF insolubles</td>
</tr>
<tr>
<td>Orr et al. (1995) [107]</td>
<td>Waste APC plastic (Table 2.4)</td>
<td>No catalyst</td>
<td>27 cm³ (batch, glass tubing in tubing bomb reactor, shaking type)</td>
<td>( F/C = 5:1 ), ( t = 20–60 ) min, ( p_{\text{H}_2,O} = 5.27–8.38 ) MPa, ( T = 300–375°C )</td>
<td>Conversion: THF insoluble solid residue Gas Oil: cyclohexane solubles Liquid: THF solubles</td>
</tr>
<tr>
<td>Venkatesh et al. (1995) [75]</td>
<td>HDPE ((M = 125000, \rho = 0.95)), PP ((M = 250000, \rho = 0.85, \text{isotactic})), PS ((M = 280000))</td>
<td>ZrO₂/SO₄, 0.5%Pt/ZrO₂/SO₄, 2.0%Ni/ZrO₂/SO₄, 0.5%Pt/ZrO₂/WO₃ ((S_g = 102.5, 1.63%S)), 1.0%Pt/γ-Al₂O₃ ((S_g = 62.0, 7.07%W))</td>
<td>27 cm³ SS (batch, tubing bomb, shaking type)</td>
<td>( F/C = 5:1 ), ( t = 20–60 ) min, ( p_{\text{H}_2,O} = 5.27–8.38 ) MPa, ( T = 300–375°C )</td>
<td>Conversion: solid residue Gas</td>
</tr>
<tr>
<td>Venkatesh et al. (1996) [76]</td>
<td>HDPE ((M = 250000, \rho = 0.96)), PP ((M = 250000, \rho = 0.85, \text{isotactic})), PS ((M = 280000))</td>
<td>ZrO₂/SO₄, 0.5%Pt/ZrO₂/SO₄, 2.0%Ni/ZrO₂/SO₄, 0.5%Pt/ZrO₂/WO₃ ((S_g = 102.5, 1.63%S)), 1.0%Pt/γ-Al₂O₃ ((S_g = 62.0, 7.07%W))</td>
<td>27 cm³ SS (batch, tubing bomb, shaking type)</td>
<td>( F/C = 5:1 ), ( t = 20–60 ) min, ( p_{\text{H}_2,O} = 5.27–8.38 ) MPa, ( T = 300–375°C )</td>
<td>Conversion: solid residue Gas Liquid</td>
</tr>
<tr>
<td>Nakamura and Fujimoto (1996) [81]</td>
<td>PP</td>
<td>No catalyst</td>
<td>75 cm³ SS (batch, shaking type)</td>
<td>( F = 10 ) g, ( F/C = 33:3:1 ), ( t = 60 ) min, ( p_{\text{H}_2,O} = 3.0 ) MPa, ( T = 380–400°C )</td>
<td>Solid residue: n-pentane insolubles Gas Oil: n-pentane solubles Liquid GC</td>
</tr>
<tr>
<td>Authors</td>
<td>Type of Plastic</td>
<td>Catalyst</td>
<td>Reaction Conditions</td>
<td>Yield</td>
<td>Analysis</td>
</tr>
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</tr>
<tr>
<td>Liu and Meuzelaar (1996) [83]</td>
<td>Waste plastic (Table 2.3)</td>
<td>No catalyst</td>
<td>Fe₂O₃/SO₄, 0.5%Pt/Al₂O₃/SO₄, Al₂O₃/SO₄, ZrO₂/SO₄, NiMo/Al₂O₃+S, SiO₂–Al₂O₃ (25%SiO₂–75%Al₂O₃), HZSM-5</td>
<td>High pressure thermogravimetric analyzer (TGA), F = 0.035 g, C = 10–50%, pH₂ = 6.31 MPa</td>
<td>TGA</td>
</tr>
<tr>
<td>Ibrahim et al. (1996) [85]</td>
<td>Waste APC plastic (Table 2.4) Elemental S Nanoscale Al₂O₃</td>
<td>ESR cell</td>
<td>20 cm³ SS (batch, tubing bomb reactor)</td>
<td>C = 10–20%, pH₂ = 3.55 MPa, T = RT–450°C</td>
<td>ESR spectroscopy</td>
</tr>
<tr>
<td>Joo and Curtis (1996) [108]</td>
<td>PS, LDPE, PET</td>
<td>NiMo/Al₂O₃ (2.72%Ni–13.16%Mo, presulfided)</td>
<td>50 cm³ (batch, tubing bomb, shaking type)</td>
<td>F = 3.5 g, F/C = 99:1, t = 60 min, pH₂,0 = 8.3 MPa, T = 430°C</td>
<td>Conversion: THF insolubles Gas Oil: n-hexane solubles Liquid: THF solubles Simulated distillation</td>
</tr>
<tr>
<td>Feng et al. (1996) [90]</td>
<td>Waste APC plastic (Table 2.4)</td>
<td>No catalyst</td>
<td>HZSM-5 (Si/Al = 80/20), SiO₂–Al₂O₃ (Si/Al = 85/15)</td>
<td>50 cm³ (batch, tubing bomb, shaking type)</td>
<td>Total yield: THF insoluble solid residue Oil: n-pentane solubles Liquid: THF solubles Simulated distillation</td>
</tr>
<tr>
<td>Zmierczak et al. (1996) [79]</td>
<td>PS (M = 280000), PS (M = ~800)</td>
<td>No catalyst</td>
<td>ZrO₂/SO₄ (Sₖ = 115), Fe₂O₃/SO₄ (Sₖ = 70)</td>
<td>50 cm³ (batch stirred type)</td>
<td>Conversion: THF+MeOH insoluble residue (centrifuged) Gas: Liquid N₂ GC GC-MS Gas Oil: n-pentane solubles Coke GC-FID Simulated distillation</td>
</tr>
<tr>
<td>Ochoa et al. (1996) [82]</td>
<td>MDPE (M = 60000)</td>
<td>No catalyst</td>
<td>A₁₂O₃ (Sₖ = 150), 75%SiO₂–25%Al₂O₃ (Sₖ = 277), 25%SiO₂–75%Al₂O₃ (Sₖ = 238), 50%SiO₂–50%Al₂O₃ (Sₖ = 250), SiO₂ (Sₖ = 187), HY zeolite (Sₖ = 872), ZCAT (25%HZSMS, Sₖ = 40)</td>
<td>25 cm³ SS (batch, tubing bomb, shaking type)</td>
<td>F = 2.5 g, F/C = 9:1, t = 15–60 min, pH₂,0 = 1.4–5.5 MPa, T = 420°C</td>
</tr>
<tr>
<td>Luo and Curtis (1996) [88]</td>
<td>PIP (M = ~800000, ρ = 0.910), PS (M = 239700, ρ = 1.050), LDPE (M = ~100000, ρ = 0.915), HDPE (M = 1250000, ρ = 0.950)</td>
<td>No catalyst</td>
<td>Fe-Naphthenate+S (1000 ppm Fe+6000 ppm S), Mo-Naphthenate+S (1000 ppm Mo+6000 ppm S), Montmorillonite, Carbon black, Low Alumina (Sₖ = 404)</td>
<td>20 cm³ SS (microtubular, shaking type)</td>
<td>20 cm³ SS (microtubular, shaking type)</td>
</tr>
<tr>
<td>Luo and Curtis (1996a) [89]</td>
<td>HDPE</td>
<td>Low Alumina ($S_g = 404$)</td>
<td>20 cm$^3$ SS (microtubular, shaking type)</td>
<td>$F = 2.0$ g</td>
<td>Conversion: THF insolubles</td>
</tr>
<tr>
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</tr>
<tr>
<td>LDPE</td>
<td>Octacat ($S_g = 268$)</td>
<td></td>
<td></td>
<td>$C = 4.9:1$</td>
<td></td>
</tr>
<tr>
<td>PET</td>
<td>Octacat-5G ($S_g = 308$)</td>
<td></td>
<td></td>
<td>$t = 30$ min</td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>50%HDPE+30%PET+20%PS</td>
<td></td>
<td></td>
<td>$p_{H_2,0} = 2.3$–8.6 MPa</td>
<td></td>
</tr>
<tr>
<td>Ibrahim and Seehra (1997) [86]</td>
<td>HDPE</td>
<td>Elemental S</td>
<td>ESR cell</td>
<td>$C = 10$%–20%</td>
<td>ESR spectroscopy</td>
</tr>
<tr>
<td>Huffman et al. (1997) [96]</td>
<td>Waste APC plastic (Table 2.4)</td>
<td>NiMo/Al$_2$O$_3$</td>
<td></td>
<td>$p_{H_2} = 3.55$ MPa</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HZSM-5</td>
<td>No catalyst</td>
<td>$T = RT$–450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Waste APC plastic (Table 2.4)</td>
<td>HZSM-5</td>
<td></td>
<td>$F = 10$ g</td>
<td>Conversion: THF solubles</td>
</tr>
<tr>
<td></td>
<td>Waste DSD plastic (Table 2.4)</td>
<td>ZrO$_2$/WO$_3$</td>
<td>50 cm$^3$ (batch, tubing bomb, shaking type)</td>
<td>$F/C = 24$–99:1</td>
<td>Gas: Liquid N$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ferrihydrite-CA (Ferrihydrite treated with citric acid)</td>
<td></td>
<td>$t = 30$–60 min</td>
<td>Oil: n-pentane solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5%Mo/Ferrihydrite</td>
<td></td>
<td>$p_{H_2,0} = 1.48$–7.0 MPa</td>
<td>Liquid: THF solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO$_2$–Al$_2$O$_3$</td>
<td>TiO$_2$–SiO$_2$ (Ti/(Ti+Si) = 0.85)</td>
<td></td>
<td>Simulated distillation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TiO$_2$–SiO$_2$ (Ti/(Ti+Si) &gt; 0.85)</td>
<td></td>
<td></td>
<td>GC-MS</td>
</tr>
<tr>
<td>Ding et al. (1997) [78]</td>
<td>HDPE ($M = 125000$)</td>
<td>TiCl$_3$</td>
<td>27 cm$^3$ SS (batch, tubing bomb, shaking type)</td>
<td>$F = 2.0$–20 g</td>
<td>Solid residue</td>
</tr>
<tr>
<td></td>
<td>Waste APC plastic (Table 2.4)</td>
<td>HZSM-5 (35%binder; Si/Al mole ratio = 35)</td>
<td>150 cm$^3$ SS (batch stirred autoclave)</td>
<td>$F/C = 20$–50:1</td>
<td>Gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No catalyst</td>
<td></td>
<td>$t = 60$ min</td>
<td>Oil: n-pentane solubles</td>
</tr>
<tr>
<td>Ding et al. (1997a) [92]</td>
<td>Waste APC plastic (Table 2.4)</td>
<td>No catalyst</td>
<td>27 cm$^3$ SS (batch, tubing bomb, shaking type)</td>
<td>$F = 2.0$ g</td>
<td>Conversion: n-pentane insolubles</td>
</tr>
<tr>
<td></td>
<td>Waste DSD plastic (Table 2.4)</td>
<td>KC-2001 (presulfided)</td>
<td></td>
<td>$F/C = 20$–40%</td>
<td>Gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.6%Ni/HSiAl (presulfided)</td>
<td></td>
<td>$t = 60$ min</td>
<td>Oil: n-pentane solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Where, HSiAl (4:1 mixture of SiO$_2$–Al$_2$O$_3$ and HZSM-5) and HZSM-5 (10–40%binder, pore size = 6.2 Å, $S_g &gt; 200$)</td>
<td></td>
<td>$T = 375$–480°C</td>
<td>GC-FID</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO$_2$–Al$_2$O$_3$ (13%Al$_2$O$_3$, pore size = 65 Å, $S_g = 475$)</td>
<td></td>
<td>$p_{H_2,0} = 7.0$ MPa</td>
<td>GC-MS</td>
</tr>
<tr>
<td>Ding et al. (1997b) [91]</td>
<td>HDPE ($M = 125000, \rho = 0.95$)</td>
<td>No catalyst</td>
<td>27 cm$^3$ SS (batch, tubing bomb, shaking type)</td>
<td>$F = 2.0$ g</td>
<td>Conversion: n-pentane insolubles</td>
</tr>
<tr>
<td></td>
<td>Waste APC plastic (Table 2.4)</td>
<td>KC-2600 (NiMo/zeolite and/or NiMo/Al$_2$O$_3$, hydrocracking catalyst)</td>
<td></td>
<td>$C = 20$–40%</td>
<td>Gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.6%Ni/HSiAl (presulfided)</td>
<td></td>
<td>$t = 0$–60 min</td>
<td>Oil: n-pentane solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Where, HSiAl (4:1 mixture of SiO$_2$–Al$_2$O$_3$ and HZSM-5) and HZSM-5 (10–40%binder, pore size = 6.2 Å, $S_g &gt; 200$)</td>
<td></td>
<td>$p_{H_2,0} = 1.83$–7.0 MPa</td>
<td>GC-FID</td>
</tr>
<tr>
<td>Authors and Year</td>
<td>Plastic Type</td>
<td>Catalyst Details</td>
<td>Conversion Details</td>
<td>GC-MS/Simulated distillation</td>
<td>Notes</td>
</tr>
<tr>
<td>------------------</td>
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</tr>
<tr>
<td>Rothenberger and Cugini (1997) [94]</td>
<td>HDPE ($\rho = 0.96, T_m = 135°C$)</td>
<td>No catalyst</td>
<td>43 cm$^3$ SS</td>
<td>CO:H$_2$ mixture as 1:1 mol%</td>
<td>GC-MS Simulated distillation</td>
</tr>
<tr>
<td></td>
<td>PS ($\rho = 1.0, T_m = 95°C$)</td>
<td>13X (Pore size = 10 Å)</td>
<td>$C = 0.7$ g</td>
<td>Conversion: THF solubles</td>
<td>Gas Oil: n-heptane solubles</td>
</tr>
<tr>
<td></td>
<td>PET ($\rho = 1.4, T_m = 215°C$)</td>
<td>AO-60 (aged, NiMo/Al$_2$O$_3$)</td>
<td>$t = 60$ min</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PP ($\rho = 0.94, T_m = 176°C$)</td>
<td>No catalyst</td>
<td>$\rho_{H_2,O} = 7.0$ MPa</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.6%Ni-7.0%Mo/HSiAl (presulfided)</td>
<td>For HSiAl see Ding et al. [93]</td>
<td>$T = 430–445°C$</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>HDPE ($M = 125000, \rho = 0.959, T_m = 130°C$)</td>
<td>No catalyst</td>
<td>50 cm$^3$ (batch stirred autoclave)</td>
<td>$F = 5.0–10$ g</td>
<td>Conversion: solid residue</td>
</tr>
<tr>
<td></td>
<td>PP ($M = 250000, \rho = 0.900, T_m = 189°C, isotactic$)</td>
<td>Fe$_2$O$_3$/ SO$_3$</td>
<td>$t = 30–180$ min</td>
<td>$F/C = 2–100:1$</td>
<td>Liquid</td>
</tr>
<tr>
<td></td>
<td>PBD ($M = 197000, \rho = 0.910, T_s = 140–170°C$)</td>
<td>ZrO$_2$/ SO$_3$</td>
<td>$\rho_{H_2,O} = 3.55–10.4$ MPa</td>
<td></td>
<td>GC-FID GC-MS</td>
</tr>
<tr>
<td>Shabtai et al. (1997) [80]</td>
<td>HDPE ($M = 125000$)</td>
<td>ZrH supported on SiO$_2$-Al$_2$O$_3$</td>
<td>482 cm$^3$ glass vessel</td>
<td>$F = 115$ mg</td>
<td>Simulated distillation</td>
</tr>
<tr>
<td></td>
<td>PE (formed in-situ)</td>
<td>IR cell</td>
<td>$F/C = 1.64:1$</td>
<td></td>
<td>GC</td>
</tr>
<tr>
<td></td>
<td>PE ($M = C18–C50$)</td>
<td></td>
<td>$t = 900–3720$ min</td>
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<tr>
<td></td>
<td>LDPE ($M = 125000$)</td>
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</tr>
<tr>
<td></td>
<td>PP ($M = 250000, \rho = 0.910, T_m = 189°C, isotactic$)</td>
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<tr>
<td>Dufaud and Basset (1998) [99]</td>
<td>PE</td>
<td>No catalyst</td>
<td>50 cm$^3$ (batch, tubing bomb reactor)</td>
<td>$F = 6.0$ g</td>
<td>Unreacted plastic: THF insolubles but decalin solubles@140°C</td>
</tr>
<tr>
<td></td>
<td>PE ($M = C18–C50$)</td>
<td></td>
<td></td>
<td></td>
<td>Gas Oil: n-hexane solubles</td>
</tr>
<tr>
<td></td>
<td>LDPE ($M = 125000$)</td>
<td></td>
<td></td>
<td></td>
<td>Coke: Decalin insolubles</td>
</tr>
<tr>
<td></td>
<td>PP ($M = 250000, \rho = 0.910, T_m = 189°C, isotactic$)</td>
<td></td>
<td></td>
<td></td>
<td>Simulated distillation</td>
</tr>
<tr>
<td>Ramdoss and Tarrer (1998) [106]</td>
<td>Waste plastic (Table 2.4)</td>
<td>No catalyst</td>
<td>50 cm$^3$ (batch, tubing bomb reactor)</td>
<td>$F = 10$ g</td>
<td>Conversion: THF solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$F/C = 99:1$</td>
<td>Gas Oil: n-pentane solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$t = 30–60$ min</td>
<td>Liquid: THF solubles</td>
</tr>
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<td></td>
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<td></td>
<td>Simulated distillation</td>
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<td></td>
<td></td>
<td></td>
<td>GC-MS</td>
</tr>
<tr>
<td>Joo and Curtis (1998) [95]</td>
<td>LDPE</td>
<td>Z-753 (hydrocracking catalyst)</td>
<td>~20 cm$^3$ SS (batch, tubing bomb reactor)</td>
<td>$F = 1.0$ g</td>
<td>Conversion: THF insolubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NiMo/Al$_2$O$_3$ (2.72%Ni-13.16%Mo, presulfided)</td>
<td></td>
<td>$F/C = 99:1$</td>
<td>Liquid: THF solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NiMo/zeolite (&lt; 25%MoO$_3$, 1–10%NiO, presulfided)</td>
<td></td>
<td>$t = 30–60$ min</td>
<td>Simulated distillation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10%Z-753-90%NiMo/Al$_2$O$_3$</td>
<td></td>
<td>$T = 400–430°C$</td>
<td></td>
</tr>
<tr>
<td>Shah et al. (1999) [97]</td>
<td>Waste APC plastic (Table 2.4)</td>
<td>No catalyst</td>
<td>50 cm$^3$ (batch, tubing bomb, shaking type)</td>
<td>$F = 10$ g</td>
<td>Conversion: THF solubles</td>
</tr>
<tr>
<td></td>
<td>Waste DSD plastic (Table 2.4)</td>
<td></td>
<td></td>
<td>$F/C = 99:1$</td>
<td>Gas Oil: n-pentane solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$t = 30–60$ min</td>
<td>Liquid: THF solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Simulated distillation</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>GC-MS</td>
</tr>
<tr>
<td>Authors</td>
<td>Feedstock</td>
<td>Catalyst/Zeolite</td>
<td>Reaction Conditions</td>
<td>Product</td>
<td>Analysis Method</td>
</tr>
<tr>
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</tr>
<tr>
<td>Walendziewski and Steininger (2001) [98]</td>
<td>Waste PE</td>
<td>NiW+10%HY catalyst</td>
<td>1000 cm³ (rotated batch autoclave)</td>
<td>$F = 25–100$ g</td>
<td>Liquid: bp &lt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$F/C = 99–332.3$</td>
<td>$t = 30–180$ min</td>
<td>Residue: bp &gt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$p_{H_2,0} = 2–5$ MPa</td>
<td>$T = 370–430°C$</td>
<td>GC-FID</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$F = 25$ g</td>
<td></td>
<td>Bromine number</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$F/C = 10:1$</td>
<td></td>
<td>Unreacted plastic: xylene solubles@130°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T = 435°C$</td>
<td></td>
<td>Gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$t = 120$ min</td>
<td></td>
<td>Oil: centrifuged</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$p_{H_2,0} = 6.5$ MPa</td>
<td></td>
<td>Wax: THF solubles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Coke: xylene insolubles</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>GC-FID</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Simulated distillation</td>
</tr>
<tr>
<td>Karagöz et al. (2002) [100]</td>
<td>LDPE ($M = 68500$, $\rho = 0.918–0.922$, no stabilizers or fillers)</td>
<td>DHC-8 ($S_g = 102.0$, non-noble metals/SiO₂-Al₂O₃) HZSM-5 ($S_g = 300$, SiO₂/Al₂O₃ = 216 molar) 4.13%Co/ACB ($S_g = 200.3$)</td>
<td>100 cm³ SS (batch, shaking type autoclave)</td>
<td>$F = 25$ g</td>
<td>Liquid: bp &lt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$F/C = 10:1$</td>
<td>$T = 435°C$</td>
<td>Residue: bp &gt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T = 370–430°C$</td>
<td>$t = 30–180$ min</td>
<td>GC-FID</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$p_{H_2,0} = 2–5$ MPa</td>
<td>$F = 25$ g</td>
<td>Bromine number</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Unreacted plastic: xylene solubles@130°C</td>
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<td></td>
<td>Gas</td>
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<td></td>
<td></td>
<td></td>
<td>Oil: centrifuged</td>
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<td></td>
<td></td>
<td>Wax: THF solubles</td>
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<td></td>
<td>Coke: xylene insolubles</td>
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<td>GC-FID</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Simulated distillation</td>
</tr>
<tr>
<td>Ali et al. (2004) [102]</td>
<td>PS ($M = 180000$, $\rho = 1.05$) PP ($M = 75000$, $\rho = 0.918$) LDPE ($M = 80000$, $\rho = 0.92–0.922$) HDPE ($M = 85000$, $\rho = 0.948$) PET</td>
<td>ZSM-5 ($SiO₂/Al₂O₃ = 30$ molar, $S_g = 390$) DHC-32 ($NiW/SiO₂-Al₂O₃$, $S_g = 239$, $v_p = 0.36$, presulfided) FCC (metal/zeolite-Y, $Al = 34%$, $S_g = 195$) NiMo/$γ$-Al₂O₃ ($S_g = 210$, $v_p = 0.38$, presulfided)</td>
<td>25 cm³ SS (batch stirred reactor)</td>
<td>$F = 10$ g</td>
<td>Liquid: bp &lt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$F/C = 10$</td>
<td>$T = 400–430°C$</td>
<td>Residue: bp &gt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T = 400$–430°C</td>
<td>$t = 30–60$ min</td>
<td>GC-FID</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$p_{H_2,0} = 8.3$ MPa</td>
<td></td>
<td>Bromine number</td>
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<td></td>
<td></td>
<td></td>
<td>Unreacted plastic: xylene solubles@130°C</td>
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<td></td>
<td>Gas</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>Oil: n-hexane solubles</td>
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<td></td>
<td></td>
<td></td>
<td>Wax: THF solubles</td>
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<td></td>
<td></td>
<td></td>
<td>Coke: xylene insolubles</td>
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<td></td>
<td></td>
<td></td>
<td>GC-FID</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>Simulated distillation</td>
</tr>
<tr>
<td>Hesse and White (2004) [104]</td>
<td>PE ($M = 700$, $T_m = 80–90°C$)</td>
<td>Pt-HZSM-5 (1.5%Al₂O₃, frame) Pt-HY (Pore size = 7.4 Å, SiO₂/Al₂O₃ = 5.30) Pt/HMCM-41 (17%Al₂O₃, pore size = 15–150 Å)</td>
<td>$F = 5–15$ mg</td>
<td>$F = 10$% PE</td>
<td>Liquid: bp &lt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$T = 100–400°C$</td>
<td>Residue: bp &gt; 360°C</td>
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<td>GC-FID</td>
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<td>Simulated distillation</td>
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<td>Bromine number</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gas: gas meter</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Liquid</td>
</tr>
<tr>
<td>Metecan et al. (2005) [101]</td>
<td>HDPE ($M = 234000$, $\rho = 0.964$) LDPE ($M = 213600$, $\rho = 0.915$) PP ($M = 565700$, $\rho = 0.920$)</td>
<td>DHC-8 (non-noble metals/SiO₂-Al₂O₃) HYDROBON (18%NiO/Al₂O₃) DHC-8+HYDROBON (50-50%)</td>
<td>100 cm³ SS (batch, shaking type autoclave)</td>
<td>$F = 835$ g</td>
<td>Liquid: bp &lt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$F/C = 20:1$</td>
<td>$T = 375–450°C$</td>
<td>Residue: bp &gt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T = 420°C$</td>
<td>$t = 60$ min</td>
<td>GC-FID</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$p_{H_2,0} = 5.0$ MPa</td>
<td></td>
<td>Bromine number</td>
</tr>
<tr>
<td>Mosio-Mosiewski et al. (2007) [103]</td>
<td>LDPE</td>
<td>No catalyst</td>
<td>2000 cm³ (batch stirred reactor)</td>
<td>$F = 835$ g</td>
<td>Liquid: bp &lt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NiMo/Al₂O₃ ($S_g = 260$)</td>
<td>$F/C = 49:1$</td>
<td>$T = 420°C$</td>
<td>Residue: bp &gt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$t = 120$ min</td>
<td>$p_{H_2,0} = 10$ MPa</td>
<td>GC-FID</td>
</tr>
<tr>
<td>Williams and Slaney (2007) [109]</td>
<td>HDPE PP PS PET PVC Waste DSD plastic (Table 2.4) Waste Fost Plus</td>
<td>No catalyst</td>
<td>300 cm³ SS (batch stirred reactor)</td>
<td>$F = 30–40$ g</td>
<td>Liquid: bp &lt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$t = 60$ min</td>
<td>$p_{H_2,0} = 1.0$ MPa</td>
<td>Residue: bp &gt; 360°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$T = 500°C$</td>
<td>GC-FID</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>Bromine number</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gas: gas meter</td>
</tr>
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<td>Liquid</td>
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<td>GC-FID</td>
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<td>Atmospheric distillation</td>
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<td>Solid residue</td>
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<td>Gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Liquid: dichloromethane solubles</td>
</tr>
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<td>GC-FID</td>
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<td>GC-MS</td>
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</tr>
<tr>
<td>Resin blend</td>
<td>44.4%HDPE+21.2%PP+13.3%PS+12.2%PVC+8.9%PET</td>
<td>40%HDPE+40%PP+20%PS+5%PVC+25%PET</td>
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</tr>
<tr>
<td>Catalyst</td>
<td>HUSY (Si/Al&lt;sub&gt;bulk&lt;/sub&gt; = 2.8)</td>
<td>HUSY (Si/Al&lt;sub&gt;bulk&lt;/sub&gt; = 2.8)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.5%Pt/USY (Si/Al&lt;sub&gt;bulk&lt;/sub&gt; = 2.8, Si/Al&lt;sub&gt;frame&lt;/sub&gt; = 9.0)</td>
<td>0.5%Pt/USY (Si/Al&lt;sub&gt;bulk&lt;/sub&gt; = 2.8, Si/Al&lt;sub&gt;frame&lt;/sub&gt; = 9.0)</td>
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<td></td>
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<tr>
<td></td>
<td>1.0%Pt/USY (Si/Al&lt;sub&gt;bulk&lt;/sub&gt; = 2.8, Si/Al&lt;sub&gt;frame&lt;/sub&gt; = 9.0)</td>
<td>1.0%Pt/USY (Si/Al&lt;sub&gt;bulk&lt;/sub&gt; = 2.8, Si/Al&lt;sub&gt;frame&lt;/sub&gt; = 9.0)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Reactions</td>
<td>300 cm³ SS (batch stirred autoclave)</td>
<td>300 cm³ SS (batch stirred autoclave)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Time</td>
<td>5.0 min</td>
<td>5.0 min</td>
<td></td>
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</tr>
<tr>
<td>Pressure</td>
<td>1.5‒5.5 MPa</td>
<td>1.5‒5.5 MPa</td>
<td></td>
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</tr>
<tr>
<td>Temperature</td>
<td>270–400°C</td>
<td>270–400°C</td>
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<tr>
<td>Conversion</td>
<td>unreacted plastic</td>
<td>unreacted plastic</td>
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</tr>
<tr>
<td>Product</td>
<td>Gas</td>
<td>Gas</td>
<td></td>
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<tr>
<td></td>
<td>Oil</td>
<td>Oil</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Coke (Xylene+element ana.)</td>
<td>Coke (Xylene+element ana.)</td>
<td></td>
<td></td>
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<tr>
<td>GC-FID</td>
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</tr>
</tbody>
</table>

All % values are weight percent. APC = American Plastic Council, DSD = Duales System Deustchland, ESR = electron spin resonance, FID = flame ionization detector, GC = gas chromatograph, HDN = n-hexadecane, HDPE = high density polyethylene, IR = infrared, LDPE = low density polyethylene, MDPE = medium density polyethylene, MeOH = methyl alcohol, MS = mass spectrometer, PBD = polybutadiene, PE = polyethylene, PET = polyethylene terephthalate, PIP = polyisoprene, PP = polypropylene, PS = polystyrene, PVC = polyvinyl chloride, SS = stainless steel, TGA = thermogravimetric analysis, THF = Tetrahydrofuran.

C = catalyst, g; F = feed, g; M = molecular weight, g/mol; p<sub>H2</sub> = hydrogen pressure, MPa; p<sub>H2,0</sub> = initial (cold) hydrogen pressure, MPa; p<sub>H2,T</sub> = hydrogen pressure initial but at reaction temperature, MPa; RT = room temperature, °C; S<sub>p</sub> = surface area, m²/g; t = reaction time, min; T = temperature, °C; T<sub>m</sub> = melting temperature, °C; T<sub>s</sub> = softening temperature, °C; v<sub>p</sub> = pore volume, cm³/g; ρ = density, g/cm³.
In a different group of researchers, Zmierczak et al. [79] also used solid superacids (sulfated catalysts), namely, Fe$_2$O$_3$/SO$_4$ and ZrO$_2$/SO$_4$ but for the hydrocracking of PS. Both the catalysts showed enhanced conversion over the thermal reaction. It was found that ZrO$_2$/SO$_4$ catalyst was more effective compared to Fe$_2$O$_3$/SO$_4$ giving higher conversion and higher amount of monocyclic arenes (fully depolymerized products) and lower amount of incompletely depolymerized products such as diphenylalkanes and triphenylalkanes. Experiments were also performed with low molecular weight PS ($M = 800$ g/mol) where again ZrO$_2$/SO$_4$ catalyst was found better though only slightly in converting PS to the reaction products. In the same group of Zmierczak et al. [79], Shabtai et al. [80] studied the hydrodegradation of HDPE over ZrO$_2$/SO$_4$ and Pt-loaded ZrO$_2$/SO$_4$ (0.5%Pt/ZrO$_2$/SO$_4$) catalysts. A similar observation to that of Venkatesh et al. [75] was reported by comparing the hydrocracking catalyst (0.5%Pt/SO$_4$/ZrO$_2$) and the cracking catalyst (SO$_4$/ZrO$_2$) as the total conversion was increased from 30.0 to 55.1% (350°C, 3.55 MPa H$_2$ pressure, 60 min reaction time, and 5:1 feed to catalyst ratio) when Pt-loaded catalyst was employed. Under the same conditions, for thermal hydrocracking (in the absence of a catalyst) negligible conversion of HDPE was obtained. Shabtai et al. [80] also studied the effect of catalyst (0.5%Pt/SO$_4$/ZrO$_2$) to feed ratio and, under the conditions described above, found the total conversion increased from 55.1 to 64.7% (17.4% increase in total conversion) when the catalyst to feed ratio was increased from 1:5 to 1:2.

A disposable and cheap catalyst that does not require reactivation and regeneration should be extremely useful in improving the overall economics of the plant especially when waste plastic material has harmful impurities that can badly damage a catalyst. This was the inspiration behind the work of Nakamura and Fujimoto [81] who used various types of catalysts with and without metal loadings and observed the effect of presulfidation with H$_2$S (H$_2$ and H$_2$S mixture, mole ratio 4 to 1) and addition of 0.03% CS$_2$ on hydrocracking of PP. Experiments with activated carbons alone (without metal loading) have shown that the activated carbon made from brown coal (ACC) was more active and yielded greater amount of total liquid as well as oil in the range of naphtha, kerosene, and gas oil and slightly less amount of gas compared to the activated carbon made from wood (ACW). However, both the activated carbons were found more active and selective towards oil and liquid yields than the conditions when no catalyst was employed. 5.0%Fe/ACC and 5.0%Fe/SiO$_2$-Al$_2$O$_3$ catalysts were also used for the hydrocracking reactions. It was found that 5.0%Fe/SiO$_2$-Al$_2$O$_3$ produced more solid and gaseous products and less liquid product as compared to 5.0%Fe/ACC whereas the former provided increased amount of oil yield. When CS$_2$ was
added to 5.0%Fe/SiO₂-Al₂O₃ and 5.0%Fe/ACC, in both the cases, the yield of liquid drastically increased and the corresponding solid residue was significantly reduced. However, the 5.0%Fe/ACC+CS₂ catalyst produced greater amount of oil and considerably less amount of gas compared to 5.0%Fe/SiO₂-Al₂O₃+CS₂. Compared to CS₂, the presence of H₂S with 5.0%Fe/ACC was found more effective for the liquefaction of PP and its small amount significantly contributed to the liquefaction. Experiments with CS₂ and H₂S without using a catalyst also showed considerable improvement in conversion and oil and liquid yields which suggested the authors to report that the role of sulfur compounds is not only the sulfidation of iron but they act as catalyst in the liquefaction of PP. Based on the above findings the authors concluded that, for the hydrocracking of PP, the iron supported activated carbon catalyst has a potential to be used as an excellent disposable catalyst for waste plastics liquefaction, due to its excellent activity and selectivity. The comparison between the results of Nakamura and Fujimoto [81] and the work of Venkatesh et al. [75] is difficult to carry out as quite lower catalyst concentrations (3.0%) were used by Nakamura and Fujimoto [81] compared to 16.7% used by Venkatesh et al. [75].

The catalytic cracking or hydrocracking reaction essentially requires acidic sites, therefore the knowledge of the quantity and type of acidic sites is essential in the design of a new catalytic system. This concept was conceptualized by Ochoa et al. [82] who studied the hydrocracking of medium density polyethylene (MDPE) on various catalysts mainly to observe the effect of acidity characteristics of a catalyst on the yield and quality of the oil produced. The catalytic materials along with their acidity characteristics used by Ochoa et al. [82] are listed in Table 2.2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Total acidity (mmol/g)</th>
<th>Brønsted/Lewis ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>187</td>
<td>0.001</td>
<td>0</td>
</tr>
<tr>
<td>25%SiO₂-75%Al₂O₃</td>
<td>238</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>50%SiO₂-50%Al₂O₃</td>
<td>250</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>75%SiO₂-25%Al₂O₃</td>
<td>277</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>150</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>HY</td>
<td>872</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ZCAT (25%HZSM-5+Inert)</td>
<td>40</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Ochoa et al. [82] found that pure Al₂O₃ and pure SiO₂ did not improve the conversion over thermal hydrocracking as SiO₂ had negligible acidic sites while Al₂O₃ did not contain strong
acid sites. On the other hand, for the amorphous SiO2-Al2O3 catalysts containing both the Brønsted and Lewis acid sites, it was observed that an increase in total acidity (Brønsted + Lewis) of SiO2-Al2O3 catalyst did not affect the oil yield. However, the oil yield was found to be a sole function of Brønsted acidity and generally increased with an increase in the concentration of Brønsted acid sites suggesting oil yield was not dependent on the concentration of Lewis acid sites. In comparison to oil yield, the gas yield was found relatively less affected as reported to be less than 1.0% in all the cases. In the absence of a catalyst at 420°C and 5.5 MPa H2 pressure, mostly (> 97%) linear molecules were obtained while in the presence of a SiO2-Al2O3 catalyst more branched product was obtained. Although, the boiling range (177 to 585°C) measured using simulated distillation was similar in both the cases, catalytic and non-catalytic, but a lighter product was obtained in the presence of a catalyst. With no catalyst in the reaction mixture 50vol% of the product boiled off at ~407°C, while 50vol% of the product boiled off at only ~287°C when catalyst was employed. For the three SiO2-Al2O3 catalysts used, the least acidic catalyst provided the smallest fraction of the lighter products. Compared to SiO2-Al2O3 catalysts, HZSM-5 (ZCAT) used in the study was found less active but showed better selectivity for the gasoline range product (C5–C12) whereas HY zeolite catalyst showed both the poor activity and selectivity characteristics. The coke formed on 75%SiO2-25%Al2O3 catalyst was about 14.0% as compared to ~10% for both 50%SiO2-50%Al2O3 and 25%SiO2-75%Al2O3 catalyst. HZSM-5 produced the least amount of coke as only 1.5%. This decreased amount of coke on HZSM-5 may be due to the smaller pore size of HZSM-5 which is not selective for large size coke molecules. On the similar basis, a quite high content of coke is expected on HY catalyst. Ochoa et al. [82] also studied different catalyst loadings such as 1%, 2%, 4%, and 10% to observe the effect of catalyst concentration in the feed mixture and to workout the optimum catalyst loading. It was found that for the catalyst loading below 4% the conversion increased with an increase in catalyst concentration. However, between 4% and 10% loading the catalytic degradation of MDPE remained at the same level.

A different strategy to observe the effectiveness of a catalyst was adopted by Liu and Meuzelaar [83] who investigated various catalysts for the hydrodegradation of waste plastic (Table 2.3) and HDPE in a high pressure TG/GC-MS system under 6.31 MPa H2 pressure. The TGA results of their study are shown in Fig. 2.6. The figure shows that the presence of each catalyst increases the rate of decomposition reaction of the waste plastic studied. It is observed that, for the given conditions, the cracking catalysts such as SiO2-Al2O3 (25%SiO2+75%Al2O3) and HZSM-5 showed the highest activity rates. It is also observed
that, at 420°C the activity decreased in the order of SiO$_2$-Al$_2$O$_3$, HZSM-5, pre-sulfided NiMo/Al$_2$O$_3$ mixed with SiO$_2$-Al$_2$O$_3$ (4:1 ratio), and superacids at the last. However, higher catalyst to feed ratio was set for SiO$_2$-Al$_2$O$_3$ and the mixed catalyst (50% loading) as compared to HZSM-5 and the others (10% loading). Among the solid superacids, ZrO$_2$/SO$_4$ proved to be the most effective catalyst and the activity decreased in the following order ZrO$_2$/SO$_4$ > Al$_2$O$_3$/SO$_4$ > 0.5%Pt/Al$_2$O$_3$/SO$_4$ > Fe$_2$O$_3$/SO$_4$ > no catalyst.

Table 2.3 Proximate and ultimate analyses of comingled waste plastic [84] used by Liu and Meuzelaar [83]

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed carbon</td>
<td>Carbon</td>
</tr>
<tr>
<td>0.45</td>
<td>86.3</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>99.7</td>
<td>14.0</td>
</tr>
<tr>
<td>Ash</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>1.8</td>
<td>0.05</td>
</tr>
<tr>
<td>Moisture</td>
<td>Sulfur</td>
</tr>
<tr>
<td>0.06</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
</tr>
</tbody>
</table>

![Fig. 2.6 High pressure TGA results of the decomposition of commingled waste plastic](shown in Table 2.3) in the absence and presence of a catalyst [83].
The products of the TGA system showed that in the absence of a catalyst, more uniformly distributed long straight chain aliphatics including alkenes and alkanes were produced. The presence of a catalyst such as Al₂O₃/SO₄, 0.5%Pt/Al₂O₃/SO₄, 0.5%Pt/ZrO₂/SO₄, 0.5%Pt/SiO₂-Al₂O₃, and pre-sulfided NiMo/Al₂O₃ mixed with SiO₂-Al₂O₃ resulted in the formation of more isomers of aliphatic nature and revealed that a stronger cracking catalyst produced more lighter aliphatics. These results support, as discussed above, Ochoa et al. [82] who also observed an isomerized product over a cracking catalyst and dominant presence of n-alkanes in the case of thermal hydrocracking and Venkatesh et al. [76] who suggested that a less active catalyst produced less amount of gases. It was also observed that strong cracking catalysts, e.g., SiO₂-Al₂O₃ and HZSM-5 provided a product that not only contained light aliphatics but it also had high yields of substituted aromatics. The presence of substituted aromatics was explained due to the occurrence of cyclization reactions on acid catalysts and/or due to the relatively long residence times available inside the pores of the catalysts. It was also observed that the effect of catalyst presence and type on the overall degradation was not important at very high temperatures and/or very long residence times.

Ibrahim et al. [85] and Ibrahim and Seehra [86] studied the thermal and catalytic hydrocracking using ESR (electron spin resonance) spectroscopy [87] in which free radicals were detected as they formed. Elemental sulfur (S), nanoscale Al₂O₃, NiMo/Al₂O₃, and HZSM-5 were used to observe the catalytic effects. HDPE and waste APC plastic (Table 2.4) were used and hydrogen pressure of 3.55 MPa was set in each ESR experiment. With waste APC plastic, initially at room temperature no ESR signal was detected showing absence of free radicals. In fact, in thermal hydrocracking experiments, no hint of ESR single was appeared earlier than 360°C (Fig. 2.7). However, in the presence of 10%S, 10%S+10%Al₂O₃, 10%S+10%NiMo/Al₂O₃, and 10%HZSM-5, depolymerization was detected at 280°C, 280°C, 240°C, and 380°C, respectively. HZSM-5 therefore did not reduce the depolymerization temperature and it was reported that nanoscale Al₂O₃ did not take part in the depolymerization process. The lower temperature with 10%S+10%Al₂O₃ was only due to the sulfur presence as shown in Fig. 2.7.
Table 2.4 Analyses of waste APC plastic and waste DSD plastic

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Waste APC</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>98.8</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>0.74</td>
</tr>
<tr>
<td>Ash</td>
<td>0.45</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>0.03</td>
</tr>
<tr>
<td>O(by difference)</td>
<td>0.91</td>
</tr>
</tbody>
</table>

Fig. 2.7 ESR spectra for hydrocracking of waste APC plastic under 3.55 MPa pressure: a) waste plastic alone, b) waste plastic+10%S+nanoscale Al₂O₃ [85].

These results are in accordance to the findings of Nakamura and Fujimoto [81] who proposed that a sulfur compound such as CS₂ or H₂S acts as a catalyst and its function is not only the sulfidation of a catalyst. With HDPE in the presence of 10%S, depolymerization was resulted approximately at 270°C close to the value obtained for waste plastic containing dominantly HDPE. With HZSM-5 and NiMo/Al₂O₃, reduced concentration of free radicals was observed with an increase in temperature which showed quenching of the free radicals formed, by the hydrogenation action of these catalysts. On the other hand, S was proposed to abstract hydrogen from the hydrocarbon molecules to form free radicals responsible for cracking and H₂S as a byproduct. Moreover, in the light of the work of Nakamura and Fujimoto [81] for thermal hydrocracking of PP in the presence of H₂S, it may be said that the H₂S produced as a byproduct also act as a cracking catalyst.
Luo and Curtis [88] utilized a series of slurry phase hydrogenation and cracking catalysts including Mo-naphthenate+S (1000 ppm Mo and 6000 ppm S), Fe-naphthenate+S (1000 ppm Fe and 6000 ppm S), Low Alumina, Super Nova-D, Octacat, Octacat-50G, carbon black, and montmorillonite clay to test their effectiveness towards hydrocracking of various individual plastics. The properties of some FFC (fluid catalytic cracking) catalysts employed are shown in Table 2.5. For LDPE at 400°C, 5.5 MPa H₂, and 30 min reaction time, the highest conversion of 57.9% was reported over Low Alumina catalyst (10% loading) treated with 5000 ppm Mo-napthenate. For the conditions mentioned, with carbon black (20% loading and 6.9 MPa H₂), Super Nova-D (5% loading), Octacat (5% loading), Octacat-50G (5% loading), Fe-naphthenate+S (1000 ppm Fe, 6000 ppm S, 6% loading), and Mo-naphthenate+S (1000 ppm Mo, 6000 ppm S, 6% loading) the conversions were 3.9, 12.4, 11.3, 11.1, 5.1, and 5.7%, respectively. For no catalyst conditions only 6.6% conversion was resulted. With HDPE even lower conversions were obtained in the presence of slurry phase naphthenate catalysts and in the presence of 10% montmorillonite clay only 3.6% conversion was obtained under the same conditions discussed above for LDPE. The effect of catalyst was also studied for PIP (polyisoprene) and PS. For PIP and PS very high conversions were obtained with both catalytic and thermal hydrocracking reactions and the effect of catalyst on the conversion under the conditions studied was difficult to investigate. However, with PS, the oil yield was improved by the addition of a catalyst and the oil yield was the highest with Mo-naphthenagte+S with least gas yield. For carbon black with LDPE (6.9 MPa H₂, 30 min, 400°C) increasing the catalyst loading from 20 to 40% the conversion was increased from 3.9 to 4.5% only. On the contrary, with Octacat-50G (5.5 MPa H₂, 30 min, 400°C) increasing catalyst loading from 2% to 5% slightly decreased the conversion from 13.3 to 11.1%. In another study [89] carried out by the same authors, the hydrocracking of a mixture of plastics (50%HDPE, 30% PET, and 20%PS) in the presence of FFC catalysts such as Low Alumina, Super Nova-D, and HZSM-5 was studied.
Table 2.5 Characterization of some of the catalysts used by Luo and Curtis [88] and Luo and Curtis [89]

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Composition (dry basis, wt%)</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low Alumina</td>
<td>Super Nova-D</td>
</tr>
<tr>
<td>SiO₂</td>
<td>87.0</td>
<td>55.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.8</td>
<td>41.8</td>
</tr>
<tr>
<td>Na</td>
<td>0.05</td>
<td>0.16</td>
</tr>
<tr>
<td>Fe</td>
<td>0.03</td>
<td>0.47</td>
</tr>
<tr>
<td>Re₂O₃</td>
<td>0</td>
<td>2.30</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>404</td>
<td>268</td>
</tr>
<tr>
<td>App. bulk density (cm³/g)</td>
<td>0.38</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Generally, both the conversion and oil yield decreased in the order of HZSM-5, Super Nova-D, and Low Alumina, however, gas yields were virtually unaffected by catalyst type at each hydrogen pressure studied in their work. As an example, at 440°C, 5.6 MPa H₂ pressure, 10% catalyst, and 30 min reaction time, the conversion was 75.1% over HZSM-5, 73.0% over Super Nova-D, and 68.5% over Low Alumina catalyst. Gas yield and hexane solubles were also the highest with HZSM-5. This enhanced selectivity of HZSM-5 towards lighter products was also reported by Liu and Meuzelaar [83] and Ochoa et al. [82]. The increased amount of light product on HZSM-5 may be explained by its high acidity characteristics and its shape selectivity (small pore size), however, hydrogenation ability of HZSM-5 as reported by Ibrahim and Seehra [86] may also contribute in increasing the liquefied products. Feng et al. [90] while studying the hydrocracking of waste APC plastic also found at each temperature that HZSM-5 provided better gasoline (< 200°C) and kerosene (200–275°C) yields compared to SiO₂-Al₂O₃ catalyst and no catalyst conditions. They also found that in each case, thermal and catalytic, total liquid yield was nearly the same at 445°C, however, at the lower temperature of 430°C, for both the catalysts, an improved liquid yield was obtained than that of thermal runs. Both HZSM-5 and SiO₂-Al₂O₃ offered beneficial effects on oil yield compared to thermal run but slightly lower gas yield was obtained with thermal hydrocracking at 445°C. Although, at 445 and 460°C virtually similar total liquid yield and oil yield were obtained on each of the two catalysts but the quality of the oil produced was different in each case as observed by simulated distillation. At 430°C, however, total liquid yield was much higher for SiO₂-Al₂O₃ than using HZSM-5 or no catalytic conditions.

Taking into account the consideration that a polymerization catalyst might well act as a reverse catalyst for the depolymerization of a plastic, Ding et al. [78] tested TiCl₃ (polymerization catalyst) and compared it with HZSM-5 as reported a highly selective...
catalyst by the previous researchers [82, 83, 88, 90]. Ding et al. [78] found that with HDPE, improved conversion was the result over both the catalysts compared to the thermal hydrocracking. However, only HZSM-5 provided slightly improved conversion with waste APC plastic and with TiCl₃ the conversion was found lower than that obtained with thermal hydrocracking. Clearly, TiCl₃ was not able to resist the impurities present in the waste plastic. A waste plastic material may have nitrogen, sulfur, chlorine, and other impurities which may be poisonous [91] or affect the efficiency of a catalyst. For both the plastics, HZSM-5 (although having slightly lower loading of 4% than TiCl₃ as 5%) was proved to have better activity to convert the feed material. However, HZSM-5 produced large amounts of gases and reduced amounts of oil compared to TiCl₃. TiCl₃ was found having better selectivity for the oil products. The reason for larger amount of gases produced over HZSM-5 catalyst was probably high residence time of 60 min in addition to its high activity and small pore size. With both the catalysts, the amounts of olefins were decreased to negligible amounts compared to thermal hydrocracking while the amounts of aromatics were increased. HZSM-5 decreased the amount of n-paraffins to a large extent compared to thermal as well as TiCl₃ and produced a better quality of gasoline containing more naphthenes, isoparaffins, and aromatics. The oil obtained over TiCl₃ was comprised of mostly n-paraffins and might need reforming in an additional step. It is important to mention here that Liu and Meuzelaar [83] also reported the formation of cyclization products over cracking catalysts including HZSM-5. Ding et al. [92] and Ding et al. [91] extended their work on hydrocracking of plastic materials and studied additional catalysts for the hydrocracking of HDPE, waste APC plastic, and waste DSD plastic (Table 2.4). Commercial hydrocracking catalysts, i.e., KC-2600 (possibly NiMo/SiO₂-Al₂O₃) and KC-2001, NiMo/HSiAl (HSiAl is hybrid support of HZSM-5 and SiO₂-Al₂O₃ in the ratio of 1:4), and Ni/HSiAl were used for this purpose. In the absence of a catalyst (thermal hydrocracking) only a small amount of HDPE was converted at 375°C, 7.0 MPa H₂ pressure, 60 min reaction time. On the other hand, under these conditions, the presence of each catalyst significantly increased the conversion. With 40% catalyst in reaction mixture, HDPE was converted to 90.0, 99.3, 99.6, and 66.0% over KC-2600, NiMo/HSiAl, Ni/HSiAl, and HSiAl catalyst, respectively. Clearly the use of a hydrogenation function has substantially improved the rate of the reaction. Generally, for each catalyst the oil yield was the same but higher gas yields were obtained over Ni/HSiAl compared to KC-2600 and NiMo/HSiAl for which gas yields were almost the same. For waste APC plastic, again, Ni/HSiAl was found the most active catalyst. It also produced the maximum oil yield and the lowest oil to gas ratio. For both types of plastic materials, comparing the use of
different hydrogenation metals, it was observed that Ni/HSiAl had better hydroisomerization ability while NiMo/HSiAl showed better hydrogenation ability. Generally, increasing catalyst loading from 20% to 40% increased the conversion and gas yields but decreased the oil yield and gas to oil yields were highly increased. With waste APC plastic, for Ni/HSiAl catalyst, when the catalyst loading was decreased from 20% to 10%, both the oil yield and conversion were increased. Although not expected, but slightly reduced conversion upon increasing catalyst loading was also observed by Luo and Curtis [88]. This increased conversion at lower catalyst loading may be explained on the basis of improper mixing of reaction contents in a tubing bomb reactor. Akah et al. [93] supported this reasoning and demonstrated that catalyst effectiveness is greatly improved in the presence of a right kind of agitator. In a stirred tank reactor, they found that for HDPE at 270°C and 5.5 MPa H₂ pressure a turbine agitator (not specified the type of turbine agitator, possibly straight blade) provided nearly half the conversion to that obtained with an anchor type agitator. They suggested that better mixing of the reaction contents improve the catalyst effectiveness and results in the reduction of both the reaction time and reaction temperature.

Ding et al. [91] also observed that hydrocracking reaction over Ni/HSiAl catalyst (20% catalyst loading) at 7.0 MPa H₂ pressure had also removed impurities such as S and N from the waste APC plastic and therefore Ni/HSiAl hydrocracking catalyst included the function of hydrotreating as well. The authors also employed used KC-2600, NiMo/HSiAl, and Ni/HSiAl catalysts after recalcining and resulfiding and observed that the conversion, oil yield, and gas yield were unaffected compared to the fresh catalysts. For the waste DSD plastic, the performance of KC-2001, KC-2600, and Ni/HSiAl catalysts was compared. Compared to thermal hydrocracking where only ~13% conversion was obtained at 375°C, 66.7, 30.9, and 49.9% conversion was obtained over 40% of each KC-2001, KC-2600, and Ni/HSiAl catalysts, respectively. Increasing temperature to 400°C and decreasing half the catalyst loading (20%), the conversion over KC-2001 reached to 78.7% compared to only ~36% by thermal hydrocracking. At 400°C, over KC-2001, the conversion reached to 94.0% for 40% catalyst loading. Though KC-2001 showed improved conversions, however, oil to gas ratio was relatively poor (< 1.0) on this catalyst. At 400°C, KC-2001 (20% loading) resulted 38.8% oil and 39.9% gas yield (total conversion of 78.7%) while KC-2600 gave 48.2% oil and only 15.2% gas yield (total conversion of 63.4%) under the same reaction conditions.

Rothenberger and Cugini [94] studied the hydrocracking of HDPE using molecular sieve (13X) catalyst and AO-60 (an aged Ni-Mo/SiO₂-Al₂O₃) catalyst. Using the molecular sieve catalyst higher hydrocracking rates were observed than that obtained in the absence of a
catalyst (thermal hydrocracking). The conversion at 430°C (60 min, 7.0 MPa H2 pressure) was 72.0% and 56.0% with and without the use of catalyst, respectively. However using NiMo/SiO2-Al2O3 aged catalyst (AO-60), the conversion of HDPE was only ~18% even lower than the thermal reaction. The AO-60 catalyst was therefore found highly inefficient catalyst compared to the molecular sieve catalyst. This can be expected from an aged catalyst which may have lost much of its activity and the impurities deposited on the catalyst may well hinder the rate of hydrocracking. The authors, however, suggested that the decreased activity of the aged catalyst was due to the hydrogenation ability of the NiMo/SiO2-Al2O3 catalyst which partly quenched the radicals formed during the cracking reaction. Contrary to that, Liu and Meuzelaar [83] and Ding et al. [91] found substantial enhancement in rate compared to thermal reactions when NiMo/SiO2-Al2O3 catalyst was used. Rothenberger and Cugini [94] also performed a single run in the presence of 13X with H2/CO mixture and at a temperature of 430°C (60 min, 7 MPa H2) for the hydrocracking of a mixture of plastics (50%HDPE, 35%PS, and 15%PP) and found that very high conversion of 97.0% was possible.

Joo and Curtis [95] in the same group of Luo and Curtis [88] discussed above, also employed NiMo/zeolite catalyst (presulfided) and compared the results with Z-753 (possibly NiW/zeolite) for the hydrocracking of LDPE. They found that at a lower temperature (400°C) virtually similar results were obtained with both the catalysts while at a higher temperature (430°C) Mo-containing zeolite catalyst was found more active in converting LDPE to reaction products. Higher gas yields were also obtained with Mo-containing catalyst. Moreover, Joo and Curtis [95] compared the above two zeolite catalysts with NiMo/Al2O3 and a mixture 10%Z-753-90%NiMo/Al2O3. As expected the two zeolite catalysts showed much better activity than the Al2O3 based catalyst. As Al2O3 is only a weak acid compared to a zeolite therefore it is expected that an Al2O3 catalyst will show less cracking activity than a zeolite catalyst [75, 82, 85].

In the same group of Feng et al. [90] mentioned above, Huffman et al. [96] and Shah et al. [97] compared the catalytic hydrocracking in a very small amount of catalyst (feed to catalyst ratio as 99:1) with non-catalytic thermal hydrocracking for the two waste plastic mixtures (waste APC plastic and waste DSD plastic). For the cleaner mixture (waste APC plastic) at 445°C, 60 min, and 1.48 MPa H2 the oil yields obtained from the catalytic and thermal runs were generally not different. However, the quality of oil was affected by the addition of even such a small amount of catalyst. In general, the addition of 1% catalyst considerably increased the yield of gasoline range products and the maximum of this occurred with
HZSM-5. Gas yields were somewhat higher for thermal reactions and over HZSM-5 catalyst. The above observation for HZSM-5 catalyst is in accordance to the view so far established in our discussion. Experiments performed at 435°C and 1.48 MPa hydrogen pressure revealed that the effectiveness of a catalyst was dependent on the reaction temperature. At 435°C and lesser reaction time (30 min) the effect of the type of catalyst was found more pronounced both for the oil yield and total conversion. For waste APC plastic mixture, HZSM-5 was found the most active and selective towards oil yield while 5%Mo/Ferrihydrite was found the least active as well as selective. Apart from HZSM-5 all the other catalysts produced lower total conversion as well as oil yield than even thermal hydrocracking. For the dirtier mixture (waste DSD plastic) again the addition of a catalyst was found influencing the hydrocracking reaction. The lowest conversion as well as the lowest oil yield was obtained with ZrO2/WO3 while the highest oil yield was obtained with a TiO2-SiO2 ((Ti/(Ti+Si)) = 0.85) catalyst. It was concluded by the authors that at high reaction temperatures, the catalyst loading of 1‒5% had smaller effect on the quality and quantity of oil produced. Without catalyst the temperature of 440–450°C found appropriate to get a high quality liquid fuel in sufficient quantity. Feng et al. [90] also found the addition of a catalyst not important at elevated temperature for the conversion and total liquid and oil yields, however, not for the quality of oil. Experiments at lower temperatures and with higher loadings of catalysts were probably required to have an otherwise different conclusion. A low value of catalyst loading of only 1% at elevated temperatures was probably not the way to determine and compare the effectiveness of different catalysts. Walendziewski and Steininger [98] used commercial catalyst containing NiW+10%HY for the hydrocracking of waste polythene. They observed insignificant depolymerization at 370°C and at a low reaction time (not mentioned) and probably at a catalyst loading of 0.3–1% (unfortunately, the conditions of the reactions are not well documented in the work and there is no thermal hydrocracking reaction for the comparison with the catalytic hydrocracking). The above observation may be explained by giving the reason that the cracking part (HY support) was only 10% in the commercial catalyst which significantly reduced the concentration of the cracking function and thereby decreased the cracking ability of the catalyst. Moreover, waste PE might contain impurities which could significantly affect the performance of the catalyst. At 410°C, 75.4% liquid boiling below 360°C and a large amount of gas (17.0%) was produced. The liquid product (< 360°C) contained 83.0% content boiling < 180°C and a small amount of aromatics (9.0%), which can be expected on a cracking catalyst [83, 78, 91]. At 400°C, the gas produced contained a large amount (86.7%) of saturated light gases such as methane, ethane, propane,
and butane but only 0.1% of ethylene. This may be due to the hydrogenation function of NiW which in the presence of hydrogen saturated any olefins formed during the course of hydrocracking process.

Dufaud and Basset [99] reported the depolymerization of PE and PP in the presence of hydrogen and an electrophilic Ziegler-Natta catalyst, i.e., zirconium hydride supported on silica-alumina catalyst and suggested the possibility of reversibility of the Ziegler-Natta polymerization. The in-situ formed PE or PP when heated to 150°C under 0.040 MPa hydrogen pressure the polyolefin was successfully depolymerized and in 15 h completely converted to only methane and ethane. Experiments were also performed with commercial (C18 to C50) low molecular weight PE samples and high molecular weight LDPE \((M = 125000 \text{ g/mol})\) and PP \((M = 250000 \text{ g/mol})\). With low molecular weight PE samples at higher pressure of 0.101 MPa H₂ and at the same temperature of 150°C, it was found that in 62 h all of PE was converted to light alkanes. The high molecular weight polyolefin samples were also able to be depolymerized at these very low temperature and low pressure conditions.

Karagöz et al. [100] used three catalysts, namely, DHC-8 (non-noble metals loaded on SiO₂-Al₂O₃), HZSM-5, and Co/ACB (activated carbon made from biomass) to study the hydrocracking of LDPE at 435°C (10:1 feed to catalyst ratio, 120 min, 6.5 MPa H₂). On each catalyst under these conditions, the conversion of plastic was almost completed. However, a large amount of semi-solid material was obtained with Co/ACB which showed it had decreased ability of cracking. For a high temperature of 435°C and reaction time of 120 min though everything was expected to be converted. It was found that the highest gas yield and the lowest liquid yield were obtained on HZSM-5 catalyst while the highest liquid yield and the lowest gas yield were achieved with Co/ACB. The gas yield was 59.6, 78.5, and 28.7% while liquid yield was 38.7, 19.1, and 71.4% on DHC-8, HZSM-5, and Co/ACB, respectively. The sulfur content in the liquid products resulted over Co/ACB catalyst was found lower than that of HZSM-5 and suggested that the activated carbon supported metal catalyst was able to capture sulfur compounds and therefore also acted as hydrodesulfurization (HDS) catalyst. It is important to mention here that the regeneration of a used ACB catalyst may require special procedures otherwise the carbon catalyst has to be disposed of as reported by Nakamura and Fujimoto et al. [81] for iron supported activated carbon catalysts. In a follow up work to that of Karagöz et al. [100], Metecan et al. [101] also employed DHC-8 (commercial hydrocracking catalyst) and compared it with commercial hydrotreating catalyst (HYDROBON, 18%NiO/Al₂O₃) for the hydroliquefaction of HDPE, LDPE, and PP. Generally, for each plastic, HYDROBON catalyst resulted greater liquid yield.
and less gas yield than DHC-8 and thermal hydrocracking. DHC-8 provided less liquid yield and higher gas yield than even thermal hydrocracking. DHC-8 was found to be a good catalyst in reducing the molecular weight of the liquid obtained and provided lower molecular weight product than both thermal and catalytic hydrocracking over HYDROBON catalyst. However, it produced liquid with high olefinic content as it showed high bromine number, higher than even thermal hydrocracking of PP and in some cases for LDPE. HYDROBON catalyst resulted much reduced bromine numbers compared to DHC-8 and thermal hydrocracking. At a high temperature of 450°C, all the properties and product distribution of the obtained liquid were independent of the effectiveness of catalyst used, exception was bromine number for polyolefins. These findings supported the works of Huffman et al. [96], Shah et al. [97], Feng et al. [90], and Liu and Meuzelaar [83] for the waste plastic mixture used in their study. It was concluded that another hydrogenation step was required when DHC-8 was employed as catalyst for hydroliquifaction of waste plastic whereas the naphtha obtained by using HYDROBON from hydrocracking of polyolefins found suitable to be used as feedstock naphtha. The 50-50% mixture of DHC-8 and HYDROBON catalyst was also studied in order to utilize the beneficial effects of both the catalysts. For HDPE, the liquid and gas yields were similar to that of DHC-8 while for LDPE and PP the yields generally lied in between the yields obtained over the two catalysts independently. Ali et al. [102] studied four catalysts, namely, ZSM-5, presulfided NiMo/γ-Al₂O₃, presulfided DHC-32 (NiW/SiO₂-Al₂O₃), and an FCC catalyst (metal supported zeolite Y) for the hydrocracking of HDPE, LDPE, PS, PP, and PET (at 430°C, 60 min reaction time, and 8.3 MPa H₂). Generally, the ZSM-5 catalyst was found the most active and selective towards oil produced. For the NiMo/γ-Al₂O₃ catalyst, as Al₂O₃ support is considered less acidic compared to amorphous SiO₂-Al₂O₃ and zeolites therefore one expects supported alumina catalyst not a good choice for cracking and hydrocracking reactions as pointed out by Venkatesh et al. [75] for 1.0%Pt/Al₂O₃ and Ochoa et al. [82] and Ibrahim et al. [85] for pure Al₂O₃. However, the reactions carried out by Ali et al. [102] are at relatively high temperature and for a long period of time, one can expect high conversion even in the presence of a less active catalyst. Moreover, as NiMo/γ-Al₂O₃ was presulfided, the presence of sulfur may well play a role in showing the cracking activity [81] for the Al₂O₃ support. The above discussion can be extended by looking at the work of Mosio-Mosiewski et al. [103] who used NiMo/Al₂O₃ for studying the hydrocracking of LDPE. The results of Mosio-Mosiewski et al. [103] are shown in Table 2.6.
Table 2.6 Findings of Mosio-Mosiewski et al. [103] for thermal and catalytic hydrocracking of LDPE. $T = 420^\circ$C, $t = 120$ min, $H_2$ pressure at the start of reaction at $420^\circ$C = 10 MPa, feed to catalyst ratio = 49:1

<table>
<thead>
<tr>
<th>Results</th>
<th>Catalytic hydrocracking (Ni-Mo/Al$_2$O$_3$ catalyst)</th>
<th>Thermal hydrocracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction products (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas products</td>
<td>5.9</td>
<td>8.6</td>
</tr>
<tr>
<td>Gasoline</td>
<td>10.0</td>
<td>14.5</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>26.2</td>
<td>34.2</td>
</tr>
<tr>
<td>Vacuum gas oil</td>
<td>29.1</td>
<td>24.2</td>
</tr>
<tr>
<td>Vacuum residue</td>
<td>28.9</td>
<td>18.5</td>
</tr>
<tr>
<td>Reactions products (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-alkane</td>
<td>79.9</td>
<td>39.5</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>1.6</td>
<td>17.3</td>
</tr>
<tr>
<td>Iso-alkanes</td>
<td>13.1</td>
<td>22.8</td>
</tr>
<tr>
<td>Alkenes</td>
<td>0.0</td>
<td>15.1</td>
</tr>
<tr>
<td>Aromatics</td>
<td>0.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Unidentified</td>
<td>5.4</td>
<td>4.7</td>
</tr>
<tr>
<td>Bromine number (units)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>&lt;1.0</td>
<td>23.4</td>
</tr>
<tr>
<td>Gasoline</td>
<td>1.5</td>
<td>68.9</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>&lt;1.0</td>
<td>26.2</td>
</tr>
<tr>
<td>Vacuum gas oil</td>
<td>2.1</td>
<td>12.3</td>
</tr>
</tbody>
</table>

$t = \text{time, min}; T = \text{temperature, } ^\circ\text{C}$

It is clearly seen that overall conversion is virtually same in both the non-catalytic and catalytic hydrocracking. Now as Al$_2$O$_3$ has reduced acidity, it also has less isomerized product and a considerably reduced ratio of iso-alkanes to n-alkanes. Moreover, the absence of aromatics also hints low activity of this type of catalyst [83, 78, 91]. However, due to the strong hydrogenation function of NiMo as pointed out by Ding et al. [91] negligible amount of alkenes was found in the reaction products validated by bromine number of only 1.5 g Br$_2$/g obtained with catalytic reaction as compared to 68.9 g Br$_2$/g with non-catalytic reaction. Additionally lower gas yield may also be an indication of low cracking ability and relatively superior hydrogenation function of the catalyst.

Hesse and White [104] studied the catalytic hydrocracking of polyethylene by observing temperature-dependent class-specific evolution profiles obtained from mass spectra. The catalysts employed were bifunctional hydrocracking catalysts, namely, Pt/HZSM-5, Pt/HY, and Pt/HMCM-41. As expected, the hydrocracking reactions were found to accelerate in the presence of a catalyst. It was observed that olefin and alkyl aromatic yields were significantly decreased when hydrogen was used in the cracking system compared to helium atmosphere. With both the Pt/HY and Pt/HMCM-41 catalysts paraffin to olefin ratio was higher as 98.0
compared to Pt/HZSM-5 in which case it was only 18.0. With all the catalysts, the effective activation energy decreased above 240°C. The decrease in activation energy was the highest (much greater) with Pt/HMCM-41 and the lowest with Pt/HZSM-5. It was reported that catalyst pore size and acidity are the key factors in determining the amount of volatile components and the activation energies involved. Following the work of Hesse and White [104], Akah et al. [93] also studied the hydrocracking reaction over Pt containing zeolite Y catalyst. They used Pt/USY (hydrocracking catalyst) and HUSY (cracking catalyst) to study the degradation of HDPE. With HUSY, at 310°C and 5.5 MPa H₂ pressure, quite lower conversion, gas yield, and gasoline yield (higher gas to gasoline ratio greater than unity) and very high coke contents greater than three times than that formed over 1.0%Pt/USY were obtained. A large amount of coke was expected in the absence of a hydrogenation function and a zeolite having large pore size as aromatics and polyaromatics (coke precursors) are easier to form over a zeolite Y catalyst. At 270°C, decreasing Pt content from 1.5 to 0.5% on USY zeolite, virtually similar conversion, and gas and liquid yields were obtained with slight increased content of coke. This suggests an increased amount of Pt may increase the stability of the zeolite catalyst by hydrogenation of the coke precursors.

2. 2.1.2 Effect of Hydrogen Pressure

The presence of hydrogen may reduce the formation of free radicals responsible for the cracking and overcracking of a hydrocarbon molecule. Also, hydrogen may saturate the olefinic intermediates and olefinic reaction products to produce an increased amount of saturated hydrocarbons and reduced content of coke formed. It may also enhance the activity of a catalyst during the course of the reaction by renewing the active sites of a catalyst. Hydrogen pressure is therefore an important factor in determining the conversion and yield and quality of the products formed and in maintaining the activity of a catalyst.

Venkatesh et al. [75] studied the hydrocracking of HDPE at 375°C in the presence of 0.5%Pt/ZrO₂/SO₄ catalyst (16.7% catalyst loading and 25 min reaction time) to observe the effect of hydrogen pressure on the conversion and yields of the products. No significant effect was observed on the conversion of HDPE, however, lower hydrogen pressure of 5.27 MPa yielded more liquid product (79.8%) with corresponding lower gas yield (19.2%) compared to higher hydrogen pressure of 8.38 MPa that yielded 69.0% of oil and 30.0% of gas. Moreover, a change in hydrogen pressure showed slightly different boiling range of the liquid product where higher hydrogen pressure favored the production of lighter hydrocarbons. Ochoa et al. [82] also found that the hydrogen pressure somewhat increased
the yield of oil while working on the hydrocracking of MDPE over SiO$_2$-Al$_2$O$_3$ and HZSM-5. They observed nearly 10% increase in pentane solubles when hydrogen pressure was increased from 1.4 MPa to 5.5 MPa (420°C, 15 min, 9:1 feed to catalyst ratio). However, they observed negligible increase in oil yield in thermal hydrocracking (in the absence of a catalyst) for the same increase in hydrogen pressure.

Unlike Venkatesh et al. [75] and Ochoa et al. [82], Ding et al. [91], Luo and Curtis [89], and Akah et al. [93] carried out the hydrocracking reaction on more than two hydrogen pressures. Ding et al. [91] observed that the hydrocracking reaction was greatly influenced initially and the effect was decreased with further increase in hydrogen pressure. The results of Ding et al. [91] for the effect of hydrogen pressure on the conversion and yields of gas and oil are shown in Fig. 2.8.

![Fig. 2.8: Effect of hydrogen pressure on hydrocracking of waste APC plastic over Ni/HSiAl (27 cm$^3$ reactor, 375°C, 60 min, feed/catalyst = 4.0:1.0) [91].](image)

It is observed that with an increase in hydrogen pressure from 1.83 MPa to 5.27 MPa, the conversion of waste APC plastic using Ni/HSiAl catalyst at 375°C increased from 84.9% at 1.83 MPa to 98.9% at 5.27 MPa. Higher hydrogen pressure had shown no significant effect on the conversion. The oil yield somewhat followed the path of conversion while gas yield virtually remained the same. Generally, at higher hydrogen pressure, the amounts of n-paraffins, iso-paraffins, and cycloparaffins were increased while the quantities of olefins and aromatics were decreased. The results suggested the authors to conclude that hydrogenation
reactions of olefins and aromatics were improved at high hydrogen pressure to produce more n-paraffins and cycloparaffins. Contrary to Ding et al. [91], Luo and Curtis [89] for the hydrocracking of a plastic mixture (50%HDPE, 30%PET, and 20%PS) observed that with an increase in hydrogen pressure from 2.3 to 8.6 MPa, generally the overall conversion and the yield of oil first decreased and then increased while the gas yields remained relatively unaffected. As an example, for the hydrocracking reaction over HZSM-5 at 2.3, 5.6, and 8.6 MPa \( \text{H}_2 \) pressures (440°C, reaction time of 30 min, and feed to catalyst ratio of 9:1), the conversions were 87.8, 75.1, and 82.5%, respectively whereas the yields of hexane solubles were 71.1, 57.9, and 62.4% and gas yields were 10.0, 10.9, and 11.4%, respectively. Akah et al. [93] studied the hydrocracking of HDPE at three different hydrogen pressures (1.5, 3.5, and 5.5 MPa) at 270°C using 1.0%Pt/USY catalyst. Similar to Ding et al. [91], Akah et al. [93] also observed a larger change in rates of hydrocracking at lower pressures than that at higher hydrogen pressures. Increasing hydrogen pressure from 1.5 MPa to 3.5 MPa (270°C, 5.0 min, 10:1 catalyst to feed ratio), a substantial increase in conversion (45.3 to 90.0%), gas yield (10.3 to 29.4%), and gasoline yield (20.0 to 53.1%) was observed. Further increase in pressure from 3.5 MPa to 5.5 MPa, the conversion, gas and gasoline yields virtually remained constant. Akah et al. [93] also measured the yield of coke produced and found the coke content decreased continuously with an increase in hydrogen pressure. They observed nearly a three times decrease in coke content when nearly four times the hydrogen pressure was increased. This suggests that higher hydrogen pressures are required to quench the coke precursors.

Zmierczak et al. [79] for the hydrocracking of PS reported the effect of final hydrogen pressure in the range of 3.55 to 17.34 MPa. The PS conversion found to change rather linearly with final hydrogen pressure. Although, the conversion was varied notably, the product distribution was not significantly affected.

### 2.2.1.3 Effect of Reaction Time

Reaction time given to a plastic feed during a hydrocracking operation is another vital factor that decides the extent of degradation and quality and yield of the gas and liquid products. An optimized reaction time is therefore required to be worked out to have high conversions, high oil to gas ratios, and superior quality motor fuels.

Venkatesh et al. [75] observed negligible effect of reaction time from 20 to 60 min on the conversion of PP over 0.5%Pt/ZrO\(_4\)/SO\(_4\) catalyst (325°C, 8.38 MPa \( \text{H}_2 \), 5:1 catalyst to feed ratio). However, they found the selectivity of the liquid product was greatly influenced by the
reaction time. For the given reaction conditions, the selectivity to gaseous products was almost 100% at 60 min whereas at 20 min the liquid yield was about 90.0%. These results show that liquid yield substantially decreases while the gas yield significantly increases with reaction time. In another study over the same catalyst, Venkatesh et al. [76] studied the effect of reaction time on the hydrocracking of HDPE. Similar results to the above were found at both 25 and 60 min reaction times. In comparison to Venkatesh et al. [75], Shabtai et al. [80] found that increasing reaction time increased the conversion even beyond 60 min while working on the hydrocracking of PP on ZrO2/So4 catalyst (no Pt metal function) at 410°C, 10.44 MPa H2, and feed to catalyst ratio as 100:1. They observed that initially the conversion increased rapidly (at low reaction times) and then virtually remained constant, i.e., the conversion increased from 87.1% at 30 min to 97.8% at 60 min reached to 99.9% and 100% at 120 min and 180 min, respectively. The obvious reasons for the difference between the findings of Venkatesh et al. [75] and Shabtai et al. [80] are the low catalyst loading of only ~1% used by Shabtai et al. [80] in contrast to 16.7% by Venkatesh et al. [75] and the absence of a strong hydrogenation-dehydrogenation metal in the work of Shabtai et al. [80]. The importance of strong metal function together with strong acidic function towards improved hydrocracking has already been discussed in Section 2.1.2. The increased catalyst loading and strong metal function considerably reduced the reaction time for Venkatesh et al. [75] though the reaction temperature was 85.0°C less in their work. Shabtai et al. [80] also studied the hydrocracking of HDPE and, similar to the work of Venkatesh et al. [75, 76] for PP and HDPE hydrocracking, found the conversion remained virtually the same, the yield of gases increased, and the corresponding yield of the liquid decreased with reaction time. The yield of gasoline range product (C5–C12), on the other hand, first increased and then decreased with an increase in reaction time. In the same group of Shabtai et al. [80], Zmierczak et al. [79] for the hydrocracking of PS over ZrO2/So4 catalyst (20:1 feed to catalyst ratio, 375°C, and final H2 pressure of 10.44 MPa) also found an increase in conversion with an increase in reaction time where the rate of hydrocracking increased more steadily with time compared to the work of Shabtai et al. [80]. They observed 43.0, 62.0, 77.0, and 96.0% conversion at 15, 30, 60, and 120 min, respectively. Moreover, they observed that generally light gases, benzene, alkylbenzenes, and naphthalenes increased with reaction time while di- and triphenylalkanes generally decreased with reaction time.

Ochoa et al. [82] worked on the catalytic degradation of MDPE at 420°C at 5.5 MPa of H2 pressure in the presence of various silica-alumina catalysts and HZSM-5 catalyst. As shown in Fig. 2.9, they found that increasing reaction time increased the yield of oil produced
and that the oil yield increased rapidly in the start and over a few silica-alumina catalysts reached to nearly 80% in 15 min and then increased only slightly after that.

![Graph showing oil yield vs. reaction time for various catalysts](image)

**Fig. 2.9 Effect of reaction time on oil yield for various catalysts employed by Ochoa et al. [82].**

The figure suggests that for the hydrocracking reactions in the presence of SiO₂ catalyst and under no catalyst condition (thermal hydrocracking), longer residence times are required to obtain the same yield of the oil produced. These results are in disagreement to the results obtained by Shabtai et al. [80] who observed a constant decrease of hexane solubles with time. Joo and Curtis [95] and Ali et al. [102] at 430°C also observed that yield of hexane solubles increased with reaction time and appeared to be doubled when reaction time was increased from 30 to 60 min. The findings of Shabtai et al. [80], where oil yield continuously decreased (beyond 30 min), may be explained on the basis that at a very high temperature of 450°C the transition state beyond which the oil yield continuously decrease might have already been reached. Moreover, both Joo and Curtis [95] and Ali et al. [102] also observed an increase in conversion and gas yield with time (at 430°C) as suggested by Shabtai et al. [80]. At 400°C, Joo and Curtis [95] observed an unusual behavior as they observed that at this lower temperature (compared to 430°C), the conversion decreased with increasing time for each of the catalyst studied and in contrast to high temperature, at lower temperature of 400°C, the gas yield remained constant with time (30 to 60 min) while oil yield deceased with time. This behavior looks suspicious and suggests that the results at 30 min may be
Ding et al. [91] and Shah et al. [97] studied the effect of reaction time on the hydrocracking of waste APC plastic and waste DSD plastic, respectively. Ding et al. [91] studied the hydrocracking reaction over Ni/HSiAl catalyst at 375°C and 7.0 MPa H₂ with feed to catalyst ratio fairly high as 4:1. The results of Ding et al. [91] for the effect of time are shown in Fig. 2.10.

![Conversion, Oil yield, Gas yield vs. Reaction time](image-url)

**Fig. 2.10 Effect of reaction time on the conversion, oil yield, and gas yield in the hydrocracking of waste APC plastic as studied by Ding et al. [91].**

The figure shows that increasing reaction time increases the conversion, oil yield, and gas yield. The conversion, oil yield, and gas yield are initially increased slowly with time, increased more rapidly between 15 and 30 min, and beyond 30 min again slowly increased. Virtually complete conversion was obtained at 60 min. As the reaction temperature used by Ochoa et al. [82] was much higher than Ding et al. [91], at lower temperature, the cracking reactions were sluggish initially and therefore the rate of hydrocracking towards oil yield was not as fast as observed by Ochoa et al. [82]. Shah et al. [97] studied the hydrocracking reaction at 30 and 60 min with and without the addition of HZSM-5 catalyst. In both the cases, in the temperature range of 415°C to 445°C the oil yield was increased with an increase in reaction time from 30 to 60 min, however, at 445°C to 455°C, the oil yields were
virtually similar at both times. In the temperature range of 415°C to about 430°C, the effect of time was found more pronounced for the catalytic process than the thermal process.

Palmer et al. [105] studied the conversion of PP and PE (the type of PE is not mentioned) in the presence of hydrogen (3.55 MPa) but in the absence of a catalyst. It was observed by the authors that increase or decrease of PP or PE conversion with time depends upon the reaction temperature. At lower temperature of 425°C, increasing time from 5 min to 60 min increased nearly four folds the conversion for both PP and PE. At higher temperatures of 475 and 525°C, the conversion of PP decreased with increasing time while for PE at 475°C it nearly remained the same. This unusual observation is in contrast to the common understanding by which increasing reaction time should increase the conversion of an irreversible (cracking) reaction. However, this observation may be explained on the fact that the coke formed during the hydrocracking reaction was not considered in calculating the conversions. It is expected that a large amount of coke was produced at these high temperatures, especially in the absence of a hydrogenation catalyst, which remained insoluble in THF and increased the amount of solid residue. Ramdoss and Tarrer [106] also studied thermal hydrocracking but they reported the conversions based on unreacted plastic after removing coke from the solid residue. For the waste plastic mixture (waste APC plastic) studied, the authors found that at each temperature, increasing reaction time increased the conversion of waste plastic material. It was observed that the change in the rate of conversion with time was initially (in 5 min) very high and later remained virtually constant with time. The gas yield continuously increased but the heavy oil yield continuously decreased with reaction time. For light oil, generally the yield first increased and then decreased with time. These results are in accordance to the findings of Shabtai et al. [80]. Increasing reaction time also increased the coke production. As an example, nearly 8.0% coke was formed at 30 min at the highest temperature of 525°C studied in their work.

2.2.1.4 Effect of Reaction Temperature
Hydrocracking temperature is one of the most important factors that can bring about considerable change in the conversion, yield of the products, and quality of the oil produced. A large number of researchers have studied the effect of temperature over a wide range of temperature to observe how temperature influences a hydrocracking reaction.

Venkatesh et al. [75] while studying hydrocracking of HDPE in the presence of 0.5%Pt/ZrO₂/SO₄ catalyst (16.7% loading) found that higher temperature of 375°C resulted in higher conversion of 99.0% (25 min) as compared to the hydrocracking reaction at 325°C
(conversion only 25%) under the same hydrogen pressure of 8.38 MPa and even for a longer period of reaction time (60 min). Moreover, improved selectivity towards liquid products was obtained at the higher temperature though it might be due to longer residence time at the lower temperature. The authors, however, suggested that the reason for higher yields of gases at low temperature was the poor mass transfer rates at these conditions which caused additional cracking of any liquid product formed initially. Nakamura and Fujimoto [81] studied the hydrocracking of PP at two levels of temperature, 380°C and 400°C. With and without the addition of a catalyst, the conversion as well as the total liquid yield increased with increasing temperature. The gas yield also increased for the catalytic reaction but remained virtually unaffected for thermal hydrocracking. It was observed that the liquid yield increased more rapidly than the gas yield. For the catalytic reaction, the reason for the lower conversion at the lower temperature was related to the pore diameter of the activated carbon involved. It was proposed that the PP molecules or initially cracked fragments had large size and were, therefore, unable to be cracked due to the small pore size of the activated carbon catalyst. However, at the higher temperature, increased thermal cracking resulted in the formation of smaller molecules which were easier to be catalytically hydrocracked in the pores of the activated carbon. Similarly, Luo and Curtis [88] and Joo and Curtis [95] in the same group of researchers found increasing temperature increased the degradation rate. Luo and Curtis [88] for the hydrocracking of LDPE over Low Alumina catalyst found increasing temperature from 400°C to 440°C to some extent doubled the conversion and Joo and Curtis [95] found that the lower temperature of 400°C was not effective for the conversion of LDPE over NiMo/Al₂O₃ as well as Z-753 catalyst as compared to the higher temperature of 430°C. Joo and Curtis [95] also found the gas and oil yields increased with increasing temperature. Also, for the LDPE hydrocracking, Ali et al. [102] raised the temperature from 400 to 430°C over ZSM-5 and NiMo/γ-Al₂O₃ catalysts and observed, in both the cases, a substantial increase in the conversion. Again, the gas yield and oil yield were also improved on both the catalysts. Like Luo and Curtis [88] and Joo and Curtis [95], Ochoa et al. [82] also observed an increase in hydrocracking effect with an increase in temperature. They observed more than 50% increase in oil yield over silica-alumina catalysts for the degradation of LDPE used in their study when temperature was increased from 380°C to 420°C. Moreover, Rothenberger and Cugini [94] and Ding et al. [91] also found an increase in conversion with temperature. Rothenberger and Cugini [94] for the thermal and catalytic hydrocracking of HDPE and a mixed plastic feed (50%PE, 35%PS, and 15%PET), respectively found an increase in
conversion, as expected, when temperature was increased from 430 to 445°C. The gas (C1–C4) yield also increased by increasing temperature. For the waste APC plastic Ding et al. [91] also found that increasing temperature from 350°C to 375°C dramatically increased the conversion for both the catalytic and non-catalytic conditions. The oil yield and the corresponding gas yield were also appreciably increased. In another study, Ding et al. [92] found similar findings for the hydrocracking of waste DSD plastic over KC-2001 (40% loading, 60 min, 7.0 MPa H₂) and observed the conversion increased 66.7% to 94.0% when temperature was increased from 375°C to 400°C.

Orr et al. [107], Palmer et al. [105], Zmierczak et al. [79], Feng et al. [90], Shabtai et al. [80], Ding et al. [78], Ding et al. [92], Ramdoss and Tarrer [106], Shah et al. [97], Walendziewski and Steininger [98], Metecan et al. [101], and Akah et al. [93] studied the hydrocracking reaction at more than two temperatures, i.e., they studied the effect of hydrocracking temperature on the variation in change in the rate of the hydrocracking reaction. Orr et al. [107] hydrocracked the waste APC plastic in the absence of a catalyst at 400 to 430°C. They observed that the conversion rapidly increased from 400 to 430°C and then virtually remained constant after that. The gas yield slowly increased with temperature from 400 to 430°C and then increased more rapidly from 430°C to 480°C. The liquid yield, on the other hand, first increased from 400 to 430°C and then decreased rapidly to reach ~6.0% at 480°C. Palmer et al. [105] also studied the thermal hydrocracking of a few plastic materials in the temperature range of 425 to 525°C. At 5 min reaction time, the conversion of PE increased continuously with temperature while for PP it first increased and then decreased with temperature. At 60 min time, however, the conversion of both PE and PP decreased with temperature. These observations may be explained on the basis that the formation of a large amount of coke (that is a part of solid residue) as expected at these high temperatures remained unaccounted and therefore resulted in such bizarre observations. In contrast to Palmer et al. [105], Ramdoss and Tarrer [106] somewhat supported the work of Orr et al. [107] and observed for the thermal hydrocracking of a waste plastic mixture that increasing temperature rapidly increased the conversion as the conversion (based on unreacted plastic) increased greater than 90% at 475°C and then slowly increased towards completion at 525°C (97.0%). For any specific time, the conversion, gas yield, and coke formation increased with temperature whereas total oil yield decreased with temperature. Zmierczak et al. [79] over Fe₂O₃/SO₄ catalyst observed a profound effect of temperature on the conversion of PS in the low temperature range (350–400°C) whereas negligible effect on the conversion was observed at higher temperatures (425–450°C), an observation similar to that made by Orr et
al. [107] and Ramdoss and Tarrer et al. [106] for thermal hydrocracking of waste APC plastic. Although, the effect of temperature was diminished at higher temperature but the quality of the product was continuously changed with temperature. The concentration of benzene plus alkylbenzenes continuously increased while the yield of diphenylalkanes and triphenylalkanes plus others continuously decreased and reached to virtually zero at 450°C. Feng et al. [90] also employed the same plastic material as used by Orr et al. [107] and observed the effect of temperature at three temperatures. Increasing temperature, generally, sharply increased the total liquid yield as well as oil yield when temperature was increased from 430 to 445°C. While increasing temperature from 445 to 460°C there was no effect on the total liquid and oil yields apart from thermal runs in which oil yield was slightly higher at 460°C compared to 445°C. Gasoline yield (BP < 200°C) generally increased with increasing temperature other than using SiO₂-Al₂O₃ catalyst in which case it was slightly decreased from going 445 to 460°C. Again, the effect was not significant beyond 445°C (except for thermal) and it was suggested that 445°C should be the maximum temperature of operation. Shabtai et al. [80] for the study of HDPE, LDPE, and PS hydrocracking over various catalysts observed in accordance to Zmierczak et al. [79] that initially at lower temperatures the conversion increased more rapidly but the effect of temperature was reduced at higher temperatures. As an example for HDPE the conversion increased from 82.5% at 420°C to 98.9% at 435°C and then reached to 100% at 450°C and 465°C. Increasing temperature increased the gas yield but decreased the oil yield for each of the plastics used. However, gasoline range product obtained from HDPE and PP first increased and then decreased with an increase in temperature. This shows that the temperature used by Shabtai et al. [80] were high enough for the catalyst employed that the oil fraction had started to convert to coke and gaseous components. Orr et al. [107] had also observed the same outcomes for high temperature thermal hydrocracking. A clue can also be obtained from the work of Palmer et al. [105] for high temperature non-catalytic hydrocracking. For the gasoline yield the results supported the work of Feng et al. [90]. Ding et al. [78] investigated the effect of temperature on HDPE and waste APC plastic material at three levels of temperature, 400, 420, and 430°C both in the presence and absence of a catalyst. In each case, increasing temperature increased the conversion and the gas and oil yields were also increased with increase in temperature. In contrast to the previous works as that of Zmierczak et al. [79] and Shabtai et al. [80] generally, the conversion increased slowly with temperature and then increased more rapidly with temperature. The gas and oil yields followed the same track. This initially reduced rate of hydrocracking compared to the work of Zmierczak et al. [79] and Shabtai et al. [80] may
be due to the decreased lower temperatures used for HDPE which is difficult to degrade at lower temperatures. In another study by Ding et al. [92], as discussed before, the effect of temperature on thermal hydrocracking of waste DSD plastic was carried out. Increasing temperature from 375°C, the conversion increased rapidly up to 450°C and then rather slowly till 480°C. This is in accordance to Zmierczak et al. [79] and Shabtai et al. [80] as compared to their previous study by Ding et al. [78]. Gas yield increased slowly in the temperature range of 375°C to 430°C and then increased more rapidly afterwards. On the contrary, oil yield increased with temperature till 430°C and followed the track of conversion, then increased slightly, and then sharply decreased to ~46% at 480°C. The decrease in the oil or liquid yield at high temperature (or on a very active catalyst or both) depending upon the plastic feed has been reported by other researchers [107, 80, 106]. The quality of the oil yield also found dependent on temperature. At 430°C and 450°C similar type of oil was produced, however, at higher temperature (480°C), a much lighter liquid was obtained. The temperature of 450°C was suggested as the optimum for thermal hydrocracking. Shah et al. [97] also used the waste DSD plastic and found that oil yield increased with increasing temperature for both catalytic and non-catalytic processes. For higher reaction time (60 min) the oil yield increased from 415°C to 435°C beyond which it stayed at the same level for both the catalytic and non-catalytic processes. However, for the lower reaction time (30 min) the effect of increase in oil yield with temperature appeared for a much higher temperature (445°C) after which the yield remained constant. Walendziewski and Steininger [98] observed that with increase in hydrocracking temperature of the waste polyethylene from 370 to 410°C, the conversion to gas and liquid products increased progressively after which it virtually remained constant showing increasing temperature beyond ~415°C did not provide any beneficial effects. The gas yield continuously increased with temperature but the liquid yield (BP < 360°C) first increased from 370°C to 390°C and then decreased with temperature. It was found that the optimum temperature for hydrocracking was 390°C resulted in the attainment of conversion higher than 90% and highest liquid to gas ratio. Metecan et al. [101] for a part of their experimental runs with HDPE, LDPE, and PP noticed that the conversion first increased and then decreased with temperature while for PP in some cases it first decreased and then increased with temperature. Also, in a few cases it increased continuously with temperature or decreased continuously with temperature. This shows every possibility. The authors also observed that increasing temperature increased the gas yield but decreased the liquid yield both in the presence and absence of a catalyst apart from PP thermal hydrocracking in which the gas yield first increased and then decreased with temperature. The quality of the products
were also affected by temperature, generally increasing temperature produced a lighter liquid and increased the yield of naphtha range product. Molecular weight of the liquids obtained decreased with temperature while bromine numbers were remained nearly the same except for PP in which case it first increased and then decreased with increase in temperature. Moreover, generally methane and ethane yields increased with increasing temperature. Akah et al. [93] studied the effect of temperature on HDPE hydrocracking over 1.0%Pt/USY catalyst at 270, 310, and 350°C. Increasing temperature from 270 to 350°C both the gas yield and conversion generally increased, while the gasoline yield and coke formation decreased with increasing temperature. The gas composition was, however, found unaltered with change in temperature (mainly C4 and negligible C1 and C2).

2.2.1.5 Effect of the Use of Different Types of Plastics

The quality and quantity of the oil obtained depend upon the type of plastic used and the conditions in which the plastic is treated. In the literature various types of plastic materials are employed by a variety of researchers to compare the effect of hydrocracking variables on the conversion, oil and gas yields, and quality of the oil produced. Both virgin and waste plastic materials are used for this purpose.

Venkatesh et al. [75] compared the hydrocracking reaction of HDPE, PP, and PS over two metal supported sulfated zirconia catalysts. They observed that PP and PS were completely converted at temperature much lower than that required for the complete conversion of HDPE. It was found that at 325°C (8.38 MPa H2, 60 min, 16.7% catalyst) over 0.5%Pt/ZrO2/SO4 catalyst only 25% of HDPE was converted whereas PP was completely degraded under these conditions. PS was completely converted even at a lower temperature of 300°C over the same catalyst, however, a comparison of PP and PS at 300°C under the same reaction conditions was not provided by the authors. For nearly complete conversions of both PP (325°C, 8.38 MPa H2, 20 min) and HDPE (375°C, 8.38 MPa H2, 25 min), for both the catalysts employed, the lower gas and the higher liquid yields were obtained when PP was hydrocracked. Moreover, the yield of C4–C12 products and the ratio of branched to normal alkane products were also higher with PP compared to HDPE [76]. However, the concentration of gasoline range products in a liquid product was much higher with HDPE. Venkatesh et al. [76] reported that the reason for the increased conversion of PP was the branching present in PP at alternate carbon atoms. Venkatesh et al. [75] also observed that the products obtained from HDPE and PP were generally gasoline range branched alkanes while PS produced benzene, alkylated aromatics, and bicyclic compounds over metal-loaded
ZrO\textsubscript{2}/SO\textsubscript{4} catalyst. At a high temperature of 440°C (30 min, 5.6 MPa H\textsubscript{2}, catalyst loading of 20%), Luo and Curtis [89] using Low Alumina catalyst (FCC catalyst) observed that PS was more difficult to be hydrocracked than that of HDPE. They observed that for HDPE, PS, and PET, the conversions were 93.3, 92.3, and 67.7%, respectively, whereas, hexane solubles, i.e., oil yields were 80.0, 63.2, and 34.1% and gas yields were 11.1, 2.9, and 25.4%, respectively. Comparing to the work of Venkatesh et al. [75], an obvious contradiction for PS and HDPE hydrocracking can be noticed. This disagreement may possibly be due to very high hydrocracking temperature involved in the latter study which resulted in a high percentage of unaccounted coke formed as conversions were based on THF insolubles. In a different study, at a lower temperature of 400°C (30 min, 5.5 MPa H\textsubscript{2}), Luo and Curtis [88] compared the non-catalytic and catalytic hydrocracking of PIP, PS, LDPE, and HDPE. For both the catalytic and non-catalytic hydrocracking as expected HDPE was the most difficult polymer to be hydrocracked. These results are, unfortunately, not in favor to their previous work [89] but support the work of Venkatesh et al. [75]. The conversions obtained were 98.9, 98.2, 6.6, and 3.0% for PIP, PS, LDPE, and HDPE, respectively under non-catalytic conditions. Virtually similar conversions to that of non-catalytic hydrocracking were obtained over the catalysts used in their study. In the same group of Luo and Curtis [88, 89], Joo and Curtis [108] studied the hydrocracking of PS, LDPE, and PET in the presence of presulfided NiMo/Al\textsubscript{2}O\textsubscript{3} catalyst (430°C, 8.3 MPa H\textsubscript{2}, 60 min, 1% catalyst concentration). Under the conditions of reactions, the order of conversion was 99.1, 95.7, and 65.3% for PS, PET, and LDPE, respectively. These results are again in disagreement to what Luo and Curtis [89] found in their study and suggest that PET is also less difficult to be hydrocracked than LDPE (or HDPE). However, similar to Luo and Curtis [88] and to the work of Venkatesh et al. [75], PS was observed to be the easiest to be hydrocracked while LDPE was found to be the most difficult to be converted. PS produced the highest oil yield (95.3%) and the least gas yield (2.7%) whilst PET gave very high gas yield of 25.9% compared to oil yield of only 57.6%. PS also produced the lightest oil fraction while LDPE provided the heaviest of oils.

Shabtai et al. [80] studied the hydrocracking of HDPE, PP, and polybutadiene (PBD) in the absence and presence of a catalyst (ZrO\textsubscript{2}/SO\textsubscript{4}). Similar to Venkatesh et al. [75] who also used ZrO\textsubscript{2}/SO\textsubscript{4} (metal-loaded) catalyst, it was found that HDPE was more difficult to be hydrocracked than PP. Moreover, in accordance to Venkatesh et al. [75], for virtually the same conversion (98.9% for HDPE at 435°C and 99.8% for PP at 400°C), PP produced less gas yield and higher liquid yield as well as higher amount of gasoline range (C5–C12) product. For the same conditions of operation, PBD was 98.5% converted at 415°C while PP
was converted to 97.8% at 410°C and with PBD less gas yield and less liquid yield was obtained under these conditions. The hydrocracking of HDPE at 450°C in the presence of Fe₂O₃/SO₄ gave normal and branched paraffins, 5- and 6- ring non-substituted ring and mono-, di-, and tri-alkyl substituted cycloparaffins. Small amounts of olefins and cycloolefins were also there. With PP at 410°C, branched paraffins, branched olefins, and polymethyl-substituted naphthenes and with PBD at 415°C, paraffins and alkyl-substituted naphthenes, benzene, alkylbenzene, tetralins and indanes, and bicyclic arenes were produced. Ali et al. [102] used five polymeric materials and four different catalysts to study the hydrocracking reaction. For each catalyst, PS was found the most easily degradable plastic and completely converted under the conditions studied whereas HDPE and LDPE were the most difficult to be converted. The order of the ease of conversion for each catalyst was PS > PET > PP > LDPE & HDPE. These results support the findings of Venkatesh et al. [75], Luo and Curtis [88], Joo and Curtis [108], and Shabtai et al. [80]. Generally HDPE provided the highest gas yield and PS the highest liquid yield. The amount of liquid yield obtained was in the following order: PS > PP & PET > LDPE > HDPE while the gas yield followed the trend as HDPE > LDPE & PS & PP & PET. These findings also support the work of Venkatesh et al. [75], Joo and Curtis [108] and Shabtai et al. [80]. Metecan et al. [101] observed that at 375°C, both HDPE and LDPE produced waxy products with no liquid yield. On the other hand, PP was easily cracked at 375°C and greater than 86.0% of liquid yield was obtained under both thermal and catalytic reactions. Compared to PP, the naphtha range product obtained over both PEs contained more n-alkanes and less iso-alkanes. These results supported the works of Venkatesh et al. [75] and Shabtai et al. [80], however, additionally it was observed that for PP compared to PEs, temperature had little effect on the gas composition and that the liquid product from PP provided higher olefinic content and showed higher bromine numbers. Williams and Slaney [109] studied various individual plastics such as HDPE, PP, PS, PVC, and PET without adding a catalyst to the reaction system. Under the conditions of reaction (1.0 MPa H₂ pressure, 60 min, and 500°C) HDPE and PP were completely degraded to oil and gas products (surprisingly no residual solid, i.e., coke). PVC and PET were difficult to be converted to liquid or gas products. The residue left (including any coke formed) was 0, 0, 22.0, 52.0, and 41.0% for HDPE, PP, PS, PVC, and PET, respectively. These observations are in contrast to the other researchers as discussed above. However, again due to very high temperature of 500°C and long reaction time, the coke formed for PS and PET wrongly presented the conversion values as conversions were based on DCM solubles which did not dissolve the coke formed. The liquid yields were 95.0, 95.0, 77.0, 2.0, and 27.0% and gas
yields were 5.0, 5.0, 2.0, 38.0, and 32.0% for HDPE, PP, PS, PVC, and PET, respectively. Very high liquid/gas ratios were obtained with PE, PP, and PS while PVC and PET produced very large amounts of gases. Very high gas yields with PET were also observed by Joo and Curtis [108]. Akah et al. [93] studied hydrocracking of HDPE, PP, and PS at a low temperature of 310°C, hydrogen pressure of 5.5 MPa, 5 min reaction time, and over 1.0% Pt/USY catalyst. Virtually complete conversion of each HDPE, PP, and PS was obtained. It was observed that high yield of C6 hydrocarbons were obtained with PP. HDPE yielded relatively higher amounts of C4 and C5 whereas PS yielded mostly C3, C4, C7, and C9. Their results also supported much of the previous studies.

In addition to the above researches a few investigations on mixture of virgin or waste plastics are also carried out. Rothenberger and Cugini [94] compared the hydrocracking reaction of HDPE and a plastic mixture (50% HDPE, 35% PS, and 15% PET) at 430°C over AO-60 catalyst. It was found that adding 50% PS plus PET to HDPE, the conversion was increased from 17.9% to 59.0%. That was expected as observed by many other researchers that PS and PET are easier to be degraded than HDPE. Liu and Meuzelaar [83] compared the hydrocracking of HDPE and a waste plastic mixture (Table 2.3) over SiO2-Al2O3 and HZSM-5 catalysts in a high pressure TG analyzer. The decomposition decreased in both the cases and similar TG profiles were obtained for both the plastics over both the catalysts. However, thermal degradation of HDPE was found to occur faster than that of waste plastic mixture. The presence of substituted aromatics in the HDPE products suggested that the aromatics present in the cracked products of the waste plastic mixture can come from the cracking of HDPE and not necessarily require polystyrene as a component. Ding et al. [78] also used HDPE and a waste plastic mixture (waste APC plastic) to study the hydrocracking reaction. Similar to Liu and Meuzelaar [83], it was found that without a catalyst, waste plastic was better converted compared to HDPE but with catalysts the opposite was true. As suggested by Ding et al. [78] the presence of heteroatoms and trace metals that are harmful for the catalysts might be the reason for this observation. At 435°C where appreciable conversions of both plastics were obtained not very different conversions, oil yields, and gas yields were obtained for each plastic. Under these conditions, HDPE, in the absence of a catalyst, yielded more olefins and less aromatics. HDPE provided more aromatics and less n-paraffins in the presence of HZSM-5 while it produced reduced amount of aromatics and increased amount of n-paraffins in the presence of TiCl3. In another study, Ding et al. [91] studied the same comparison over some other catalysts and again found that waste APC plastic was easier to be converted in thermal hydrocracking, as found in their previous study, giving roughly three
times the conversion and the liquid yield at 375°C. Moreover, in contrast to their previous work for each of the catalyst used, waste APC plastic provided better conversion and liquid yields, however, the product distribution was similar for both types of plastics. Huffman et al. [96] and Shah et al. [97] compared two types of waste plastics, one washed and cleaner (waste APC plastic) and the other unwashed and dirtier (waste DSD plastic). At 435°C, for each catalyst, waste DSD plastic was found easier to be cracked and produced more pentane solubles than waste APC plastic mixture, while at 445°C, waste APC plastic was found easier to be cracked and produced more total liquid product as well as pentane solubles. However, generally at 445°C, waste DSD plastic produced more light liquid (gasoline range product, IBP-200°C) while waste APC plastic provided more heavy fraction (≥ 275°C). The quality of the oil produced by the type of catalyst used was observed to be affected only for the waste APC plastic. Similar to Huffman et al. [96] and Shah et al. [97], Ding et al. [91, 92] also found that waste APC plastic was easier to be hydrocracked under the conditions studied in their work. In the presence of a catalyst such as NiHSiAl (40% loading) and KC-2600 (40% loading) greater than 90.0% conversion was obtained and equal to or greater than 42.0% oil yield was obtained with waste APC plastic at 375°C compared to only 30.9 and 49.9% conversion and 20.7 and 35.1% oil yield over KC-2600 and Ni/SiAl, respectively for the waste DSD plastic. At 375°C, however, a slightly increased conversion in thermal hydrocracking was obtained with DSD. Comparing their previous work with waste APC plastic, thermal hydrocracking was found more effective for waste DSD plastic at each temperature studied.

Williams and Slaney [109] studied the thermal hydrocracking of a simulated waste mixture and compared its results with two actual waste plastic mixtures, i.e., waste DSD plastic and waste Fost Plus plastic. The two waste plastic mixtures yielded 48.2% and 70.6% liquid, 2.2% and 4.9% gas, and 35.1% and 17.8% residue, respectively. The simulated waste mixture contained HDPE (44%), PP (21.2%), PS (13.3%), PVC (12.2%), and PET (8.9%). Based on the results with individual plastics as discussed before, they calculated the liquid yield as 75.1%, gas yield as 11.1%, and residue as 12.9%. However, the experimental results showed that liquid yield, gas yield, and residue were 55.8%, 4.4%, and 22.7%, respectively. These findings show the possible interactions present among the individual plastics when they are hydrocracked in a mixture and to some extent discourages the possibility, as suggested by Akah et al. [110], that the product distribution can be controlled by adjusting the composition of a feed mixture.
2.2.2 Mechanisms and Kinetics Involved in Hydrocracking of Plastics

The hydrocracking of a plastic material may be explained by the two most common mechanistic pathways, one that requires the formation of free radicals and the other that involves the formation of carbocationic ions (carbocations). In the radical mechanism which may occur in thermal hydrocracking or hydrocracking over a solid that contains weak or no acid sites, e.g., activated carbon, alumina, and TiCl₃, the intermediate free radicals are formed by thermolytic process and/or by hydrogen abstraction by the support [81, 100]. A free radical is unstable and undergoes cracking (α- or β-scission) reaction to produce an olefin and another free radical. Termination of a free radical may occur through radical coupling (recombination), hydrogen abstraction, or disproportionation reaction [78, 79, 111]. On an acidic catalyst such as HZSM-5, a carbenium ion may be formed by hydrogen abstraction caused by the acid sites of the catalyst. The carbenium ion may undergo further acid catalyzed reactions such as isomerization and cracking at the β-position (β-scission) to produce an olefin and a smaller carbenium ion. The olefin produced may be hydrogenated in the presence of a high hydrogen partial pressure before appearing in the product slate. However, the presence of Brönsted sites may bring about proton transfer which leads to the formation of a less likely [112] pentacoordinated carbonium ion which can undergo β-scission to produce smaller paraffinic molecules and carbenium ions [113]. On a hydrocracking catalyst that contains both hydrogenation-dehydrogenation and acid sites, the hydrocarbon is dehydrogenated on a metal site to produce an olefin. The olefin is then moved to an acid site and protonated and isomerized. The protonated branched olefinic species undergoes β-scission (acid catalyzed reaction) and the cracked unsaturated species diffuses to a hydrogenation site and therefore a saturated hydrocarbon is the result. In the presence of both catalytic cracking and hydrocracking catalysts, other acid catalyzed reactions such as dehydrocyclization reactions can also occur. Hydrocracking reaction may also be possible on a catalyst containing a hydrogenolysis metal such as Rh, Ir, Os, etc., supported on a non-functional support, where breaking of C–C linkages may occur together with the hydrogenation of the product species [114]. It is important to mention here that even in the presence of an acid (cracking) catalyst or a hydrocracking catalyst, the formation of free radicals formed by thermal energy addition may not be ruled out but may be required to start the catalytic reaction [103, 83], i.e., initially large polymer molecules are broken down into smaller fragments [81] which are further catalyzed to produce cracked products.

In comparing the role of Pt and Ni loaded over sulfated zirconia Venkatesh et al. [76] found that increased isomerization occurred with Ni than Pt at 375°C. It was reasoned by
Venkatesh et al. [76] that metal function dissociates molecular hydrogen into atomic form to give hydride ions. The intermediate carbenium ions formed by the acidic sites can possibly react with a hydride ion and therefore desorbed to the gas phase as products. Greater the amounts of hydride ions lesser will be isomerization as intermediate carbonations live for shorter time. As Ni is less active than Pt, it produces reduced amount of hydride ions and therefore offers greater residence time to carbocations to undergo isomerization. For activated carbon alone (no metal function) Nakamura and Fujimoto [81] suggested that cracking ability of an activated carbon catalyst means its ability to abstract hydrogen especially tertiary hydrogen (PP) from a hydrocarbon species. A large hydrocarbon molecule may be formed by thermal cracking initially and interacts with the catalyst and hydrogen is abstracted on the catalyst surface giving rise to a hydrocarbon radical which further undergoes β-scission to form an olefin and another hydrocarbon radical as shown in Fig. 2.11 below.

For a metal supported activated carbon, Nakamura and Fujimoto [81] reported, and supported by Karagöz et al. [100], that the metal function dissociates hydrogen molecule into hydrogen atoms, the hydrogen may quench the free radicals formed by hydrogen abstraction or themolytic process to avoid overcracking or saturate olefins to produce a product with reduced olefins and lighter components [100]. The authors suggest that the present mechanism is different from the usual hydrocracking mechanism occurs on hydrocracking catalysts. It is a radical decomposition mechanism that does not involve carbenium ion intermediate as formed on an acidic support but occurs through hydrocarbon radical formation.

In the absence of a catalyst while comparing the cracking of HDPE in the presence of nitrogen and hydrogen, Ding et al. [78] suggested hydrogen as a chain transfer agent which may undergo chain transfer reaction and saturate the radicals formed by thermal decomposition and therefore prevent further bond scission. Rothenberger and Cugini [94]
also suggested the same mechanism for HDPE cracking in the presence and absence of a catalyst. This simple mechanism is shown in Fig. 2.12.

\[
\begin{align*}
R - CH_2 - CH_2 - CH_2 - CH_2 - CH_2^+ + H_2 & \\
\rightarrow R - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 + H^* &
\end{align*}
\]

\[
\begin{align*}
R - CH_2 - CH_2 - CH_2 - CH_2 - CH^+ + N_2 & \\
\rightarrow R - CH_2 - CH_2 - CH_2 - CH^+ + CH_2 = CH_2 (\beta \text{- scission}) &
\end{align*}
\]

Fig. 2.12 Comparison of the presence of hydrogen and nitrogen for the non-catalytic cracking reaction.

Based on the high gas yield obtained over HZSM-5 for HDPE cracking, Ding et al. [78] suggested that hydrocracking of HDPE involved carbocations. On the contrary, over TiCl₃, HDPE hydrocracking was suggested to follow free radical mechanism with recombination and disproportionation as the chain termination steps [115]. Metecan et al. [101] studied two commercial catalysts, a hydrotreating catalyst (HYDROBON) which may have a stronger hydrogenation function, and a hydrocracking catalyst (DHC-8) which may have a stronger acidic function (SiO₂-Al₂O₃ compared to Al₂O₃). For the hydrocracking of HDPE, two different mechanisms were suggested for the two catalysts. A carbenium ion mechanism as discussed above was suggested for DHC-8 (stronger acidic function) while radical mechanism was reported for HYDROBON catalyst where hydrogen may be dissociated by the hydrogenation metal and therefore can quench free radicals and saturate olefins as discussed above. Mosio-Mosiewski et al. [103] supported the free radical mechanism on metal supported alumina support while studying the hydrocracking of LDPE. It was reasoned that alumina has only weak acid sites which render it not to give rise to a carbenium ion mechanism. For the hydrocracking of HDPE over metal supported catalysts, Ding et al. [91] presented the carbenium ion mechanism and stated that in the absence of a metal function the rate of formation of carbenium ion was lower on the hybrid support as the intermediate olefins were not formed which would ultimately decrease the HDPE conversion. However, the results showed the statement only true for the commercial hydrocracking catalyst, KC-2600 (possibly NiMo/SiO₂-Al₂O₃). The high gas yield obtained in the study was explained on the basis of pentacoordinated carbonium ion mechanism. However, disproportionate reactions were also suggested to occur. In a disproportionation reaction alkylation of an olefinic intermediate and adsorbed carbenium ion occurs, the cracking of which results in a
higher carbon number species and a lower carbon number species carbon number lower than the reactants. Hesse and White [104] also suggested disproportionation to occur at low temperature more often than β-scission reactions.

Shabtai et al. [80] reported the carbenium ion mechanisms for both polyethylene and polypropylene hydrocracking. Their mechanisms are shown in Fig. 2.13 and Fig. 2.14. For PP, in the presence of strong acid sites tertiary carbenium ions are formed. The carbenium ions formed are cracked at the beta position to generate olefins and lower molecular weight carbenium ions. These smaller carbenium ions undergo metathesis reaction with molecular hydrogen to produce a lower molecular weight paraffin hydrocarbon. Additional cracking reactions can further reduce the length of the hydrocarbons. The olefin formed in the cracking process is readily protonated and undergoes metathesis reaction with hydrogen to produce the corresponding paraffin product. For HDPE, the hydrocarbon molecule is protonated and cleaved to produce an alkene and a smaller carbenium ion. The hydride and alkide shifts produce branching in the hydrocarbon molecule and results in lower molecular weight branched paraffin.

![Mechanism of PP hydrocracking described by Shabtai et al. [80].](image-url)
Fig. 2.14 Mechanism of the formation of branching in HDPE described by Shabtai et al. [80].

Dufaud and Basset [99] proposed a reaction mechanism for polyethylene hydrogenolysis by an electrophilic zirconium hydride on silica-alumina Ziegler-Natta polymerization catalyst. The mechanism is outlined below [99, 116] and schematically shown in Fig. 2.15.

- Activation of C–H bond in polymer chain
- The chain is linked to the center of Zr
- β-alkyl transfer to produce an alkyl-olefin complex
- Hydrogenolysis of the complex to produce a hydrido-olefin complex and a smaller paraffin molecule
- Olefin insertion results in the formation of an alkyl complex
Hydrogenolysis of the complex leads to the separation of catalyst and the formation of another saturated hydrocarbon molecule.

Fig. 2.15 Mechanism of polythene hydrogenolysis proposed by Dufaud and Basset [99].

Only a single study on the kinetics of hydrocracking of plastics has been found in the literature. Ramdoss and Tarrer [106] studied kinetics of waste APC plastic mixture at various temperatures and reaction times. Based on the mechanism proposed (shown in Fig. 2.16), the following five differential equations (Eq. 2.1 to Eq. 2.5) were developed assuming each of the reactions was first order with respect to mole fraction of the corresponding species.

\[
\frac{dP}{dt} = -k_1P - k_2P - k_3P \\
\frac{dH}{dt} = k_1P - k_4H - k_6H - k_7H \\
\frac{dL}{dt} = k_2P + k_4H - k_5L - k_8L \\
\frac{dG}{dt} = k_3P + k_5L + k_6H \\
\frac{dC}{dt} = k_7H + k_8L
\]  

Assuming Arrhenius temperature dependency of the rate constants, the values of the pre-exponential factors and activation energies of each of the reactions was figured out by solving the differential equations simultaneously and doing regression of the data. Table 2.7 shows the results of the kinetic modeling. It is shown in the table that the highest active energies
such as 121.7 kJ/mol and 113.5 kJ/mol are obtained when light and heavy liquids are converted to gaseous products, respectively, while the lowest activation energy of 11.8 kJ/mol is resulted for the case when heavy liquid is converted to light liquid.

![Fig. 2.16 Reaction pathways for hydrocracking of waste plastic mixture proposed by Ramdoss and Tarrer [106].](image)

Table 2.7 Results of kinetic modeling carried out by Ramdoss and Tarrer [106]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Pre-exponential factor (min⁻¹)</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4612</td>
<td>62.9</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>34.7</td>
</tr>
<tr>
<td>3</td>
<td>70792</td>
<td>86.3</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>11.8</td>
</tr>
<tr>
<td>5</td>
<td>4.8×10⁶</td>
<td>121.7</td>
</tr>
<tr>
<td>6</td>
<td>3.5×10⁵</td>
<td>113.5</td>
</tr>
<tr>
<td>7</td>
<td>1×10⁵</td>
<td>42.6</td>
</tr>
<tr>
<td>8</td>
<td>1803</td>
<td>81.1</td>
</tr>
</tbody>
</table>

Only a few of the researchers studied the effect of reaction time on the hydrocracking reaction but they did not kinetically model their findings. In the present study, the experimental data of Ding et al. [91] is used to carry out a simplified kinetic modeling. The weight percent conversion of plastic material was fitted with an appropriate mathematical function and the derivative of the function obtained at a given time was used to find the rate of the reaction at that time. The rate and fractional conversion were related by the following simple power law equation (Eq. 2.6) for an irreversible reaction. By fitting of the rate and conversion data the overall rate constant and overall order of the reaction were calculated. The results of kinetic modeling are shown in Table 2.8.
\[ \frac{dX_A}{dt} = (-r_A) = kX_A^n \]  \hspace{1cm} (2.6)

Where, \((-r_A)\) is rate of reaction of plastic \((A)\) degradation in \(s^{-1}\), \(k\) is rate constant in \(s^{-1}n^{-1}\), \(X_A\) is conversion in wt\%, and \(n\) is order of reaction.

Table 2.8 Results of kinetic modeling for the experimental data of Ding et al. [91]

<table>
<thead>
<tr>
<th>(N)</th>
<th>Function</th>
<th>Constants</th>
<th>(k) ((s^{-1}n^{-1}))</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>(X = \exp(a + bt + ct^2 + dt^3))</td>
<td>(a = 2.593517117)</td>
<td>(b = 0.097409994)</td>
<td>(c = -0.00161467)</td>
</tr>
</tbody>
</table>

\(N\) is number of data points, \(X\) is conversion (wt\%), and \(t\) is time (min). Feed = waste APC plastic, catalyst = Ni/HSiAl (4:1 mixture of SiO\(_2\)-Al\(_2\)O\(_3\) and HZSM-5), feed/catalyst = 1.0/0.2, temperature = 375°C, cold hydrogen pressure = 7.0 MPa.

2.3 Outcome of the Literature and its Relevance to the Present Study

The review of the literature has revealed that the presence of a catalyst is essential in decreasing the temperature as well as time for the hydrocracking reaction. A catalyst is desired in order to control the gas, oil, and total liquid yields. Also the quality of these products, importantly, the quality of the oil fraction can be significantly improved by the use of a suitable catalyst. It is observed that a range of catalysts has been employed by various researchers in the field. However, micro-mesoporous catalysts or mesoporous catalysts with induced activity have not been used for the hydrocracking of plastic molecules. Among the catalysts employed, the microporous zeolite catalysts have been found highly active, but, more selective towards gaseous product. Microporous zeolite materials are good in a sense as they have high acidity and therefore cracking ability but owing to the nature of small pores of these materials they hinder the access of large plastic molecules to much of the active sites present within the pore structure. Moreover, small openings of these materials offer shape selectivity and a large amount of smaller molecules (gases) are evolved. In order to address these issues, composite catalysts comprising the benefits of microporous activity and mesoporous accessibility and mesoporous catalysts with induced acidity are required to be studied for the hydrocracking of plastic molecules.

Regarding kinetics of the hydrocracking reaction, only one study is found where kinetics of the reaction is described. However, this study is carried out in the absence of a catalyst. Kinetic modeling for the catalytic hydrocracking of plastics is therefore also missing from the
literature. The concept of a commercial facility for continuous waste plastic hydrocracking is also not found in the literature.

References


[115] A. Holmström, E.M. Sorvik, Thermal degradation of polyethylene in a nitrogen atmosphere of low oxygen content. II. Structural changes occurring in low-density
polyethylene at an oxygen content less than 0.0005%, Journal of Applied and Polymer Science Appl Polym Science. 18 (1974) 761–768.

Chapter 3
Experimental Details

Hydrocracking of plastic materials was studied in two high pressure autoclave reactors. A number of in-house and commercial catalysts with and without metal impregnation were synthesized, characterized, and tested for the hydrocracking reaction. The details of the development of catalysts, experimental setup, and procedure for the catalytic runs are described in the following sections.

3.1 Experimental Setup
The experimental setup consisted of a high pressure cylindrical batch reactor vessel, a high capacity heater to heat the reactor vessel, an agitator system for thorough mixing of the reaction contents, pressure and temperature gauges, and temperature control mechanism to maintain the temperature at a desired level. The schematic diagram of the experimental system is shown in Fig. 3.1. Two different size autoclave reactors, provided by Parr Instrument Co., were used to carry out the hydrocracking reactions. The two reactor systems were essentially similar apart from the size of the reactor vessel and pressure and stirring display modules. Reactor 1 (Model 4568) had a bigger 650 ml stainless steel cylinder while Reactor 2 (Model 4562) had a smaller 500 ml stainless steel cylinder. The actual photographs of the two reactor systems are shown in Fig. 3.2.

In each of the reactor systems, a high capacity heater was used to uniformly heat the cylindrical walls and the bottom of the reaction vessel. The heater was able to slide up and down on its support rod to permit easy access to the vessel. Inside the reaction vessel, an agitator assembly was installed to effectively disperse the catalyst particles throughout the reaction mixture. The agitator was made to work on the principle of attachment of the stirrer shaft to an inner set of magnets. A J type thermocouple in a 1/8 in (3.175 mm) diameter stainless steel sheath was equipped for measuring the temperature of the reactor. A stainless steel Bourdon gauge was there to indicate the pressure inside the reactor. An inlet gas valve was located at the top (head) of the reactor which was connected to the dip tube extended to the point near the bottom of the cylinder. The liquid sampling valve was attached to the same fitting as that of the gas inlet valve and was connected to the same dip tube. The dip tube was therefore capable of withdrawing liquid product when there was gas pressure in the reactor. There was also a gas release valve to take out the gas sample from the reactor vessel. The leakage between the reactor vessel and reactor head was avoided by using a flexible form of
graphite seal. There was a safety rupture disc attached to the head which was intended to rupture and release the pressure before it reached a dangerous level. Both reactors had a reactor temperature controller that had microprocessor based control module that provided PID control with adjustable tuning parameters. The temperature was controlled by providing the set point. The control panel contained a heater switch with three positions that controlled the amount of power sent to the heater. It also contained an on-off switch and a speed (rpm) control knob. The control panel of Reactor 1 was different than control panel of Reactor 2. Both reactors had similar temperature display and setting module but Reactor 1, additionally, had digital read outs for pressure in the reactor and stirring speed (rpm) of the agitator.

Fig. 3.1 Schematic diagram of the experimental setup.
3.2 Experimental Procedure
Weighed amounts of plastic material and catalyst were introduced directly into the reactor vessel. The catalyst was dried previously in an oven at 130°C for 30 min to remove the moisture contents. The vessel was joined tightly with reactor head and the heater was raised to cover the body of the vessel. A desired initial hydrogen pressure was then given to the reactor. The pressure given was monitored for a specified time to rule out any possible gas leakage from the reactor. A certain temperature set point was given to the reactor and the heater switch was then turned on. Typically, the reactor achieved the temperature set point within 45 min, depending on the final temperature required. When the temperature reached the desired reaction temperature, reaction time was started. The reaction was carried out for the specified time of reaction after which the furnace was turned off and lowered to expose the reactor vessel to the surrounding air. This was done to quickly cool down the reaction contents to stop the cracking reaction. The reactor was allowed to cool down to the room temperature. The gas release valve was cracked open to collect the gaseous products. The reactor vessel was then removed and the liquid and solid products were collected.

3.3 Product Analyses
The reaction products were analyzed by solvent extraction method as shown in Fig. 3.3. A calculated amount of n-heptane was added to the contents of the reaction products after the
gases are removed. The n-heptane solubles were considered as “oil”. The n-heptane insolubles are then dissolved in tetrahydrofuran (THF). The sum of these THF solubles and n-heptane solubles together were called as “liquid”. The THF insoluble solid residue (catalyst, coke, and unreacted plastic) left after drying in oven at 110°C was named “solids”. The reaction conversion was based on this dried solid residue. The yields of the products and conversion were therefore defined as:

\[
\text{Oil yield} = \frac{\text{weight of n-heptane solubles}}{\text{weight of plastic fed to the reactor}} \times 100
\]

\[
\text{Liquid yield} = \frac{\text{weight of total THF solubles}}{\text{weight of plastic fed to the reactor}} \times 100
\]

\[
\text{Solids yield} = \frac{\text{weight of dried solid residue}}{\text{weight of plastic fed to the reactor}} \times 100
\]

\[
\text{Gas yield} = 100 - (\text{oil yield} + \text{liquid yield} + \text{solids yield})
\]

\[
\text{Conversion} = \frac{\text{weight of plastic fed} - \text{weight of dried solid residue}}{\text{weight of plastic fed to the reactor}} \times 100
\]

The oil produced (n-heptane solubles) were also analyzed by gas chromatography. For this Shimadzu GC-2014, with FID detector was used. Teknokroma TRB-1 capillary column (100% dimethylpolysiloxane) with 100 meter length and 0.25 mm of inner diameter was used. The temperature of injector was set at 300°C whereas the detector was at 310°C. Nitrogen was used as a carrier gas with purity of 99.999% (Linde). The initial column temperature was 45°C. The column temperature was then increased to 220°C at the rate of 7°C/min. An isothermal time of 2 min was given at 220°C and then the temperature was increased to 260°C where 10 min isothermal time was given. Then again at the rate of 7°C/min to reach at 290°C. Here again 30 min retention time is given. In each case 1 µL injection was given by autosampler. Split ratio of 24 and column flow was 1.77 mL/min. Standard solutions upto C16 were used to identify the range of the peaks.
3.4 Experimental Program

In the first stage, all the catalysts without metal impregnation were tested for their activity under identical experimental conditions shown in Table 3.1. All these reactions were performed in Reactor 2. However, experiments on USY modified catalysts and Al-modified mesoporous catalysts were performed in Reactor 1.

Table 3.1 Experimental parameters for the evaluation of catalyst activity for preliminary experiments (first stage of experiments)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model plastic mixture, wt%</td>
<td>40% HDPE, 10% LDPE, 20% PS, 30% PP</td>
</tr>
<tr>
<td>Initial cold H₂ pressure, bar</td>
<td>20</td>
</tr>
<tr>
<td>Reaction temperature, °C</td>
<td>350–425°C</td>
</tr>
<tr>
<td>Feed to catalyst ratio, g/g</td>
<td>10:0.5</td>
</tr>
<tr>
<td>Residence time, min</td>
<td>60</td>
</tr>
</tbody>
</table>
The best performing five catalysts with respect to both conversion and liquid yield were selected for the second stage of experiments. In the second stage of experiments, additional experiments were performed over the best catalysts. HDPE and actual waste plastic mixture were used as feed and the reactions were carried out at a single temperature of 400°C. Experiments were also performed on one of the best catalysts to observe the effect of operating parameters such as temperature, initial cold hydrogen pressure, catalyst concentration, and reaction time. Using the above data obtained at various operating conditions, kinetics of the hydrocracking of model plastic mixture was carried out. Table 3.2 shows the ranges of operating conditions for the second set of experiments. All these reactions were also carried out in Reactor 2.

Table 3.2 Range of operating parameters for second stage of experiments

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic HDPE</td>
<td>Model plastic mixture (Table 3.1)</td>
</tr>
<tr>
<td></td>
<td>Waste plastic mixture (40% HDPE, 10wt% LDPE, 20wt% PS, 30wt% PP)</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>350, 375, 400, 425</td>
</tr>
<tr>
<td>Initial H(_2) (cold) pressure, bar</td>
<td>10, 20, 30</td>
</tr>
<tr>
<td>Feed to catalyst ratio, g/g</td>
<td>20:1, 33.3:1, 100:1</td>
</tr>
<tr>
<td>Residence time, min</td>
<td>7.5, 30, 50, 60, 90</td>
</tr>
</tbody>
</table>

The stability of these five catalysts was also studied by hydrocracking the model plastic mixture (Table 3.1). One set of experiments was studied by using 50% of coked catalyst and 50% of fresh catalyst. Second set of experiments was performed on 50% of calcined coked catalyst (calcined in static air at 600°C for 5 h) and 50% of fresh catalytic support. Mixing of the fresh catalyst was deliberately done to maintain the same amount of feed and feed to catalyst ratio while keeping the same reaction conditions. All reactions were performed at fixed conditions of 400°C, initial cold H\(_2\) pressure of 20 bar, 10:0.5 (g/g) as feed to catalyst ratio and residence time of 60 min. These experiments were also performed in Reactor 2.

In addition to that, in order to study the effect of the presence of hydrogenation-dehydrogenation function, the best performing five catalyst supports were impregnated with 0.5wt% Pt and further experimentation was carried. Moreover, additional binary and ternary metal mixtures were impregnated on one of the best performing catalyst supports and hydrocracking reactions were performed. Model plastic mixture (Table 3.1) was selected for
these experiments and lower temperatures such as 325°C, 350 °C, and 375°C were used at 20 bar initial cold H₂ pressure. The feed to catalyst ratio was maintained as 10:0.5 (g/g) and 60 min of residence time was given. However, one experiment at 375°C was also performed with actual waste plastic mixture over one of the best Pt impregnated catalysts. These experiments were carried out in Reactor 2.

3.5 Materials

Both virgin and waste plastic materials were used for the hydrocracking reactions. Virgin plastics such as high density polyethylene (HDPE, ρ = 0.952 g/cm³), low density polyethylene (LDPE, ρ = 0.918 g/cm³, MP = 100–125°C), polypropylene (PP, MW = 250,000 g/mol, ρ = 0.9 g/cm³), and polystyrene (PS, MW = 192,000 g/mol) were obtained from Sigma-Aldrich and employed for the hydrocracking reactions. Waste plastics such as HDPE (Head & Shoulders Shampoo bottles washed, cleaned, and dried), LDPE (unused plastic bags used for shopping), PP (unused boxes used for takeaways), and PS (unused tea cups), all obtained from the local market.

Sodium hydroxide, cetyltrimethylammoniumbromide (CTAB,≥99%), tetrapropyl ammonium bromide (TPAB, 98%), tetraethylorthosilicate (TEOS, 98% purity), aluminum isopropoxide (≥98% purity), Pluronic P123, Pluronic F127, NH₄F (≥98%), ammonium acetate (≥98%), HCl (35.4% purity), NH₄OH (33% NH₃, Riedel-deHaën), aluminum nitrate nanohydrate (≥98%), tetraammineplatinum(II) chloride hydrate (99.99%), cobalt(II)nitrate hexahydrate (≥98%), ammonium meta tungstate hydrate (≥99.0%), ammonium molybdate tetrahydrate (99%), ruthenium(III) chloride hydrate, tetraaminepalladium(II) chloride monohydrate (≥99.99%), and Nickel(II) nitrate hexahydrate (99%) were required for the synthesis of catalysts. All these chemicals except HCl were also purchased from Sigma-Aldrich. HCl was purchased from BDH Chemicals. n-heptane (99%, Lab-scan) and tetrahydrofuran (THF, 99.9%, Sigma-Aldrich) were used for solvent extraction. Pyridine (≥99%, Sigma-Aldrich) was used for py-FTIR analysis. All of the solutions were made in double distilled water. Three commercial zeolite catalysts, namely, CBV720, CP811C-300, and CBV2314 were used for comparison and to produce their modified forms. The type and properties of these catalysts as provided by the supplier are given in Table 3.3.
Table 3.3 Commercial zeolite catalysts with their characteristic properties

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Zeolite type</th>
<th>Cation type</th>
<th>Si/Al</th>
<th>Surface area (m²/g)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBV720</td>
<td>USY</td>
<td>Proton</td>
<td>30</td>
<td>780</td>
<td>Zeolyst International</td>
</tr>
<tr>
<td>CP811C-300</td>
<td>BETA</td>
<td>Proton</td>
<td>300</td>
<td>620</td>
<td>Zeolyst International</td>
</tr>
<tr>
<td>CBV2314</td>
<td>HZSM-5</td>
<td>Ammonium</td>
<td>23</td>
<td>425</td>
<td>Zeolyst International</td>
</tr>
</tbody>
</table>

3.6 Catalyst Preparation

A variety of catalysts were prepared in order to evaluate the effect of the type of a catalyst on the hydrocracking of a plastic material. The following types of catalysts were prepared and used in the study.

- Mesoporous catalysts (Al-modified)
- Mesoporous catalysts containing zeolite nanoseeds
- USY modified catalysts (micro-mesoporous composite USY)
- HZSM-5 modified catalysts (micro-mesoporous composite HZSM-5)
- Zeolite beta modified catalysts (micro-mesoporous composite zeolite beta)
- Dual function catalysts (metal impregnated)

Below are the synthesis procedures of the above catalysts and Fig. 3.4 at the end of this section shows a typical method used in the synthesis of a zeolite composite catalyst.

3.6.1 Mesoporous Catalysts

3.6.1.1 Mesoporous SBA-16 Catalysts

Pluronic F127 was dissolved in 2.0 M HCl with continuous stirring for 1 h at room temperature. After complete dissolution, 0.1 g of NH₄F was added and the solution was allowed to stir further for 2h at 35°C. Afterwards, 6.0 g of TEOS was added into it. The mixture was hydrolyzed with vigorous stirring for 4 h at 40°C. Then, a calculated amount of aluminum isopropoxide was added for achieving Si/Al wt. ratio of 10. This solution was allowed to stir vigorously, overnight, to form ordered mesoporous structure. For hydrothermal treatment, the mixture was transferred into Teflon lined stainless steel autoclave and crystallized at 100°C in an oven for a complete day. Before transferring it into autoclave, pH value was adjusted to 7 using ammonia solution. The final product was centrifuged (Centurion, 6000 rpm) and washed several times with double distilled water. Afterwards the catalyst was dried in an oven for 20h at 100°C. The catalyst was then calcined.
for 6h in a muffle furnace at 600°C where the temperature increased from room temperature to the calcination temperature at the rate of 2°C/min. The final catalyst produced was named as Al-SBA-16(10). Al-SBA-16(20) and Al-SBA-16(40) were synthesized with the same method as that of Al-SBA-16(10) with Si/Al ratio of 20 and 40 respectively. Catalyst Al-SBA-16(10)3 was prepared with Si/Al ratio of 10, however, the pH of the mixture was maintained at 3 instead of 7 using ammonia solution and then transferred into Teflon lined autoclave for hydrothermal treatment. The remaining procedure was the same. Table 3.4 shows the Si/Al ratio of the gel along with pH of the gel maintained for these catalysts.

Table 3.4 Names of the mesoporous catalysts with their synthesis conditions

<table>
<thead>
<tr>
<th>Name of catalyst</th>
<th>Si/Al ratio (gel)</th>
<th>pH of the mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-SBA-16(10)</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Al-SBA-16(20)</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>Al-SBA-16(40)</td>
<td>40</td>
<td>7</td>
</tr>
<tr>
<td>Al-SBA-16(10)3</td>
<td>10</td>
<td>3</td>
</tr>
</tbody>
</table>

3.6.1.2 Mesoporous SBA-15 Catalyst

1M HCl solution was made and split into two parts. 35.3 g of P123 was added into 437ml of 1M HCl solution. After stirring, 0.1g of NH4F was added into this solution and stirring was continued for further 15 min at room temperature. 70g of TEOS was then dissolved in that solution and the mixture was hydrolyzed with vigorous stirring for 4 h. To achieve the Si/Al ratio of 10, calculated amount of aluminumisopropoxide was added into the remaining 219 ml of 1 M HCl solution in a separate reaction vessel and allowed to stir for 4 h. The two separately prepared solutions were then mixed together. The final solution was then stirred at 50°C for 20 h to form ordered mesoporous structure. The pH of the mixture was adjusted to 7 before transferring into Teflon lined stainless steel autoclave. The autoclave was placed into an oven for one day. The catalyst obtained was washed with double distilled water and centrifuged many times. For drying, the catalyst was placed in an oven at 100°C for 20 h. Calcination of catalyst was done for 6 h at 600°C in static air. The final product was named as Al-SBA-15.

3.6.2 Microporous-Mesoporous Composite Catalysts Containing Zeolite Nanoseeds

3.6.2.1 SBA-16 Composite Catalyst

The preparation of SBA-16 composite from zeolite nanoseeds took place in two steps. The first step involved the preparation of ZSM-5 nanoseeds. Two separate mixtures were
prepared for this purpose. In the first mixture, 20 g of TPAB was dissolved in 50 ml of water. After this, 40 g of TEOS was added into it. The mixture was hydrolyzed with vigorous stirring for 4 h at room temperature. In the second mixture, 1.5 g of NaOH was dissolved into 88 ml of double distilled water. Then, stoichiometric amount of aluminumisopropoxide was added for achieving Si/Al ratio of 20. That solution was allowed to stir for 2 h at room temperature. The two solutions were then combined and the resulting gel was vigorously stirred for 1 h. The solution was then allowed to age for 6 h at 120°C in order to make nanoseeds of ZSM-5. Separately, to form SBA-16 solution, 10 g of F127 was dissolved into 183 ml of 2 M HCl solution with continuous stirring for 4 h at room temperature. 0.1 g of NH₄F was added to this solution and allowed to stir for additional 3 h. After that, ZSM-5 nanoseed solution was added to this solution and the mixture was allowed to stir vigorously for 24 h at 36°C to form ordered mesoporous structure. The pH value of this solution was adjusted to 7 by using ammonia solution. For hydrothermal treatment, the mixture was transferred into Teflon lined stainless steel autoclave and crystallized at 120°C in an oven for 2 days. The final product was centrifuged and washed several times with double distilled water. The catalyst was dried in an oven for 20 h at 100°C. The catalyst was calcined for 5 h in a muffle furnace at 600°C with heating ramp of 2°C/min. The catalyst so synthesized had the sodium form and in order to achieve the proton form an ion-exchange procedure was performed. This procedure was done by stirring the catalyst in 100 ml of 3 M ammonium acetate solution, under vigorous stirring for 5 h at 60°C. The catalyst was then filtered and washed with double distilled water and dried in an oven at 100°C for 12 h. The catalyst was again calcined at 600°C for 4 h in a muffle furnace. The catalyst was named as MZ-16.

3.6.2.2 SBA-15 Composite Catalyst
Composites of SBA-15 with zeolite nanoseeds were prepared following the same procedure as that used for the preparation of MZ-16. However, in this catalyst, P123 was used as surfactant and 1 M HCl was used instead. The SBA-15 composite catalyst was named as MZ-15.

3.6.2.3 MCM-41 Composite Catalyst
MCM-41 composite catalyst was prepared by dissolving TPAB in double distilled water. After complete dissolution, TEOS was added into it. The mixture was hydrolyzed with vigorous stirring at room temperature. Aluminum isopropoxide was added in calculated amount in 0.1M NaOH solution for achieving Si/Al wt. ratio of 20. The two solutions were
mixed together and stirred vigorously. After this, cetyltrimethylammonium bromide (CTAB) was dissolved into the solution at room temperature. The mixture resulted was again subjected to stirring. After this the solution was allowed to age for 6h at 120°C, in order to make nanoseeds of ZSM-5. For hydrothermal treatment, the mixture was transferred into Teflon lined stainless steel autoclave and crystallized at 120°C in an oven for 2 days. The final product was centrifuged and washed several times with double distilled water. The catalyst was dried in oven for 20hr at 100°C. The catalyst was calcined for 5h in a muffle furnace at 550°C. The catalyst was ion exchanged in order to achieve proton form. The catalyst was then filtered and washed with double distilled water and dried in an oven at 100°C for 12h. The dried catalyst was calcined again at 550°C for 4h in a muffle furnace. The catalyst was named as MZ-41.

3.6.3 Modified USY Catalysts

3.6.3.1 USY/SBA-16 Composite

For the composite USY/SBA-16 catalyst, two separate mixtures were initially prepared. In the first mixture, 6 g of F-127 was dissolved in 1 M HCl solution and the mixture was allowed to stir for 4 h until a clear solution was obtained. 0.07 g of NH₄F was then added into the mixture. In the second mixture, 10 g of USY was added into double distilled water along with 12 g of TEOS and the resulting solution was stirred for 4 h at 35°C. The above two mixtures were then mixed together. The solution so obtained was then allowed to stir for 20 h at 36°C. The ammonia solution was then added dropwise to get the pH value of 3. For the hydrothermal treatment, the final solution was transferred into Teflon lined stainless steel autoclave and crystallized in an oven at 120°C for 21 h. The final product was centrifuged and washed several times with double distilled water and allowed to dry for 8 h at 100°C. The final product was calcined for 6 h in a muffle furnace at 600°C with heating ramp of 2°C/min. The catalyst was called as UC1.2, as TEOS/USY ratio was set equal to 1.2. UC0.92 and UC0.75 were also prepared by following the same procedure, however, the amount of USY zeolite used was 13 g and 16 g, respectively, in the preparation of these catalysts.

3.6.3.2 USY/SBA-15 Composite

The USY/SBA-15 composite catalyst was prepared following the same procedure as that of UC1.2, with TEOS/USY ratio of 1.2. However, in this catalyst the surface active agent P-123 was used instead of F-127. All the remaining procedure and quantities were the same. The catalyst was named as US1.2.
### Table 3.5 Names of the composite USY mesoporous catalyst along with their synthesis conditions

<table>
<thead>
<tr>
<th>Name of catalyst</th>
<th>Amount of USY</th>
<th>Surface directing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>UC1.2</td>
<td>10</td>
<td>F127</td>
</tr>
<tr>
<td>UC0.92</td>
<td>13</td>
<td>F127</td>
</tr>
<tr>
<td>UC0.75</td>
<td>16</td>
<td>F127</td>
</tr>
<tr>
<td>US1.2</td>
<td>10</td>
<td>P123</td>
</tr>
</tbody>
</table>

#### 3.6.4 Modified ZSM-5 Catalysts

##### 3.6.4.1 ZSM-5 with Mesoporous Silica

16 g of powdered ZSM-5 zeolite catalyst (CBV2314) was mixed with 1.5 M NaOH solution. The zeolite ZSM-5 was in the ammonium form therefore it was calcined previously for 5 h at 600°C in a muffle furnace at the rate of 2°C/min to obtain a proton form. The resulting solution was then allowed to stir at 40°C for 30 min. 16 g of TEOS was then added into this solution and the solution was allowed to stir for 4 h at 35°C.

In a separate vessel, 7 g of P123 was added into 1 M HCl solution and the solution was stirred for 4 h until clear solution was obtained. 0.1 g of NH₄F was then added and stirring was carried out for further for 30 min of time. The former mixture was then added to the latter mixture and the final mixture was stirred for 24 h at 40°C. For the hydrothermal treatment, the mixture was transferred into Teflon lined stainless steel autoclave and crystallized at 110°C in an oven for 24 h. Before transferring into the autoclave the pH of the resulting solution had a value of 1. Final product was centrifuged, washed several times with double distilled water. The catalyst was dried in oven for 20 h at 100°C. The catalyst was calcined for 5 h in muffle furnace at 600°C with heating ramp of 2°C/min. The catalyst synthesized had sodium form. In order to achieve the proton form the ion-exchange procedure was performed. This procedure was done by stirring the catalyst in 100 ml of 3 M ammonium acetate solution, under vigorous stirring for 5 h at 60°C. The catalyst was then filtered and washed with double distilled water, and dried in an oven at 100°C for 12 h. The catalyst was again calcined at 600°C for 4 h in a muffle furnace. The catalyst was called as ZC-P. ZC-F and ZC-FP were prepared using the same procedure, however, the template used were F127 and mixed template, respectively.
Table 3.6 Names of the composite ZSM-5 catalysts along with surface directing agent used in their synthesis

<table>
<thead>
<tr>
<th>Name of catalyst</th>
<th>Surface directing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5 (CBV-2314)</td>
<td>–</td>
</tr>
<tr>
<td>ZC-P</td>
<td>P-123</td>
</tr>
<tr>
<td>ZC-F</td>
<td>F-127</td>
</tr>
<tr>
<td>ZC-FP</td>
<td>P-123+F-127</td>
</tr>
</tbody>
</table>

3.6.5 Modified Zeolite Beta Catalysts

3.6.5.1 Zeolite Beta with Post Aluminum Impregnation

5% (by weight) of aluminum was impregnated over the zeolite beta powdered catalyst (CP811C-300). A calculated amount of aluminum nitrate nanohydrate for 5% aluminum impregnation was added in 40 ml of water. 5 g of the beta support was mixed with this solution and allowed to stir vigorously for 1 h at 50°C. The solution was then equilibrated for further 24 h at room temperature. The final aluminum impregnated zeolite catalyst was rinsed with water, dried in an oven at 100°C, and calcined at 600°C for 4 h at the rate of 2°C/min in a muffle furnace.

3.6.5.2 Zeolite Beta with Mesoporous Silica

8.28 g of a mixture of F-127 and P123 was added into 1 M HCl solution and the solution was stirred for 3 h. 0.1063 g of NH4F was then added into the solution. Separately, 1.5 M NaOH solution was prepared and 3.7 g of powdered zeolite beta (CP811C-300) was added to it and the solution was stirred for 1 h at 60°C. A third solution was prepared by adding 4.9 g of aluminumisopropoxide (AIP) into 1 M HCl solution. The resulting solution was stirred for 4 h at room temperature to have a homogenous solution. The first two solutions were mixed together and the resulting solution was stirred continuously for 15 min. 40 g of TEOS was then added into this solution. The solution was again stirred for 4 h at 50°C. After that the third mixture was poured into it and the final mixture was then continuously stirred for 24 h. For the hydrothermal treatment, the mixture was transferred into Teflon lined stainless steel autoclave and crystallized at 110°C in an oven for 27 h. Before transferring into the autoclave the pH of the mixture was maintained to 4 by the use of with ammonia solution. The final product was centrifuged, washed several times with double distilled water. The catalyst was dried in oven for 20 h at 100°C. The catalyst was then calcined for 5 h in muffle furnace at 600°C with heating ramp of 2°C/min. The synthesized catalyst had a sodium form. In order to achieve the proton form the ion-exchange procedure was performed. This procedure was
done by stirring the catalyst in 100 ml of 3 M ammonium acetate solution, under vigorous stirring for 5 h at 60°C. The catalyst was then filtered and washed with double distilled water and dried in an oven at 100°C for 12 h. The catalyst was again calcined at 600°C for 4 h in a muffle furnace. The final catalyst was called as BC11.1. Catalyst BC5.7 was synthesized using the same procedure, however, the TEOS/Beta ratio was 5.7 (wt/wt). BC0.7 and BC27 were synthesized with 0.7 M and 0 M NaOH (no sodium hydroxide), respectively, keeping all the other variables as constant. BC48 was produced from the same method as that of BC27, however, in this case the duration of hydrothermal treatment in autoclave was 48 h in contrast to 27 h used in all the other catalysts.

Table 3.7 Names of the composite beta catalysts along with their synthesis conditions

<table>
<thead>
<tr>
<th>Name of catalyst</th>
<th>Nature</th>
<th>TEOS/Beta</th>
<th>Molarity of NaOH (M)</th>
<th>Hydrothermal treatment (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B300</td>
<td>Microporous (CP811C-300)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>BAI</td>
<td>Microporous (CP811C-300) with 5wt%Al</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>BC11.1</td>
<td>Composite of CP811C-300</td>
<td>11.1</td>
<td>1.5</td>
<td>27</td>
</tr>
<tr>
<td>BC5.7</td>
<td>Composite of CP811C-300</td>
<td>5.7</td>
<td>1.5</td>
<td>27</td>
</tr>
<tr>
<td>BC0.7</td>
<td>Composite of CP811C-300</td>
<td>11.1</td>
<td>0.7</td>
<td>27</td>
</tr>
<tr>
<td>BC27</td>
<td>Composite of CP811C-300</td>
<td>11.1</td>
<td>0</td>
<td>27</td>
</tr>
<tr>
<td>BC48</td>
<td>Composite of CP811C-300</td>
<td>11.1</td>
<td>0</td>
<td>48</td>
</tr>
</tbody>
</table>

3.6.6 Bifunctional (Metal Impregnated) Catalysts

3.6.6.1 Monometallic (Platinum) Impregnated Catalysts

The best performing 5 catalysts were impregnated with 0.5wt% platinum. The catalysts selected for the platinum impregnation included ZC-P, ZC-F, ZC-FP, BC27, and BC48. A calculated amount of tetraammineplatinum(II) chloride hydrate was dissolved in 40 ml of water. 5 g of catalyst was then mixed with the solution and allowed to stir vigorously for 15 min at 40°C. NH₄OH solution was then added dropwise so that the pH of the solution became 9. Afterwards the solution was stirred for 1 h at 40°C. The solution was then allowed to equilibrate for additional 24 h at room temperature. The product was rinsed with doubly distilled water, dried in an oven at 100°C, and calcined at 500°C for 4 h.

3.6.6.2 Bimetallic and Trimetallic Impregnated Catalysts

ZC-FP catalytic support was also co-impregnated with 0.5wt% of platinum and 0.3wt% of palladium to produce 0.5%Pt-0.3%Pd/ZC-FP. Tetraammine platinum(II) chloride hydrate and
tetraammine palladium(II) chloride monohydrate were used for the impregnation of Pt and Pd. Additionally, 0.3%Pd-0.7%Ru/ZC-FP was prepared using tetraamminepalladium(II) chloride monohydrate and ruthenium(III) chloride hydrate, 10%Co-0.7%Ru/ZC-FP using cobalt(II)nitrate hexahydrate and ruthenium(III) chloride hydrate, and 7%Ni-12%Mo-15%W/ZC-FP using nickel(II) nitrate hexahydrate, ammonium molybdate tetrahydrate, and ammonium meta tungstate hydrate. In all of these catalysts, the same procedure of impregnation was adopted as that used for the monometallic platinum impregnated catalysts.

<table>
<thead>
<tr>
<th>Name of catalyst</th>
<th>Metal impregnated</th>
<th>Wt% metal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monometalic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/ZC-FP</td>
<td>Pt</td>
<td>0.5</td>
</tr>
<tr>
<td>Pt/ZC-P</td>
<td>Pt</td>
<td>0.5</td>
</tr>
<tr>
<td>Pt/ZC-F</td>
<td>Pt</td>
<td>0.5</td>
</tr>
<tr>
<td>Pt/BC27</td>
<td>Pt</td>
<td>0.5</td>
</tr>
<tr>
<td>Pt/BC48</td>
<td>Pt</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Bimetallic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt-Pd/ZCFP</td>
<td>Pt, Pd</td>
<td>0.5, 0.3</td>
</tr>
<tr>
<td>Pd-Ru/ZCFP</td>
<td>Pd, Ru</td>
<td>0.3, 0.7</td>
</tr>
<tr>
<td>Co-Ru/ZCFP</td>
<td>Co, Ru</td>
<td>10, 0.7</td>
</tr>
<tr>
<td><strong>Trimetallic</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Mo-W/ZCFP</td>
<td>Ni, Mo, W</td>
<td>7, 12, 15</td>
</tr>
</tbody>
</table>

All of the above mono-, bi-, and trimetallic supported catalysts catalysts were reduced ex-situ in the presence of hydrogen flow before using them in the autoclave reactor to carry out the hydrocracking reaction. A catalyst to be reduced was placed in a glass tube which was located inside a tubular furnace. The temperature of the furnace was increased up to 500°C and the reduction of the catalyst was carried out under hydrogen flowrate of 100 ml/min for 2 h. The temperature of the furnace was then decreased to the room temperature under hydrogen atmosphere (to avoid oxygen chemisorption at high temperature) and the reduced catalyst was then used in the autoclave reactor for the hydrocracking reaction.
3.7 Catalyst Characterization

The catalysts prepared were characterized using XRD (x-ray diffraction), SEM (scanning electron microscopy), EDX (energy dispersive x-ray) spectroscopy, FTIR (Fourier transform infrared) spectroscopy (FTIR), (py-FTIR) (pyridine Fourier transform infrared) spectroscopy, and nitrogen adsorption-desorption isotherms.

3.7.1 X-Ray Diffraction (XRD)

Low angle XRD patterns of the calcined catalysts were observed using PANanalytical Empyrean diffractometer (Cu-Kα X-ray radiations) with a step size of 0.013° and step time of 8.67 s. The 2θ angle range covered was 0.5–4°. The wide angle XRD patterns of the calcined catalysts were observed by employing PANalytical X’Pert diffractometer that uses
Ni filtered Cu-Kα radiation (λ: 0.145nm), operated at 45kV and 40mA. The scanning step used was 0.02° per step in the range of 2θ 6‒90°.

3.7.2 Scanning Electron Microscopy with Energy Dispersive X-ray (SEM with EDX) Analysis
Scanning electron microscopy images were obtained using Mira 3 TESCAN Field Emission Scanning Electron Microscope (SEM). Energy Dispersive X-ray (EDX) analysis was also carried out to measure the Si/Al ratio in the catalyst. All the samples were scanned after carbon coating (sputtering).

3.7.3 Nitrogen Adsorption Desorption
Micromeritics TriStar II-3020 (Surface Area and Porosity Analyzer) was used for obtaining the N₂ adsorption/desorption isotherms of the catalysts at 77.3 K. All the samples were degassed under vacuum at 200°C for 2 h using Micromeritics Smart Prep (Programmable Degas System) before the measurement. The total pore volume was estimated from the analysis of the amount of nitrogen adsorbed at a relative pressure (p/p°) of 0.9933 by assuming negligible adsorption on the external surface as compared to adsorption in the pores. N₂-BET surface area was calculated using Brunauer-Emmett-Teller (BET) adsorption approach. The pore surface area and pore volume were estimated by t-plot method. Barrett-Joyner-Halenda (BJH) model was used for the calculation of pore size distribution using adsorption branch of the isotherm. The estimation of the size of the mesopores was carried out using BJH procedure to the adsorption branch of the isotherm.

3.7.4 Fourier Transforms Infrared (FTIR) Spectroscopy
Infra red (IR) spectra of the calcined catalysts as well as the hexane solubles (oil) of some the specific experiments were taken at room temperature using JASCO FTIR-4100 in the range of 400‒4000 cm⁻¹. The pellets were made with KBr having 98% KBr and 2% (by weight) catalyst.

3.7.5 Pyridine Fourier Transforms Infrared (py-FTIR) Spectroscopy
Pyridine adsorbed FTIR spectroscopy was used for the analysis of type and strength of the acid sites of the catalysts. It was recorded using JASCO FTIR-4100 in the range of 1400‒1700 cm⁻¹. Self-supported wafers were produced from the powdered samples. These wafers were then treated at 130°C under vacuum for 1 h and subjected to pyridine adsorption at 60°C for 30 min. It was followed by the pyridine desorption at 300°C for 1 h.
3.7.6 Transmission Electron Microscopy (TEM)
Field emission transmission electron microscope (TEM), Joel JEM-2100F, was used to study the detailed morphology of the catalysts. Powdered samples were dispersed in ethanol and tiny drops of the suspension were placed on a copper grid and evaporated afterwards.
Chapter 4
Characterization and Hydrocracking Performance of Composites of Zeolite USY with Mesoporous Silica

In comparison to microporous zeolite catalysts, composite micro-mesoporous catalysts not only offer reduced diffusional problems but they can also be prepared with increased activity and the desired selectivity. In this chapter, the commercial USY (CBV720) and the in-house composite catalysts of the commercial USY and mesoporous SBA are characterized by various techniques and their hydrocracking performance for a model plastic mixture is studied. The catalysts are characterized by SEM analysis, nitrogen adsorption-desorption approach, small angle and wide angle XRD analyses, FTIR analysis, and Py-FTIR analysis. The catalytic activity and selectivity are evaluated at three reaction temperatures (375°C, 400°C, and 425°C) for an initial cold hydrogen pressure of 20 bar and a residence time of 60 min. The oil products obtained in the reactions are further analyzed by GC-FID. Additionally, under the same conditions of hydrogen pressure and at constant temperature of 400°C, the effect of reaction time (30 min, 60 min, and 90 min) is studied on the hydrocracking ability of the catalysts.

4.1 Catalyst Characterization
4.1.1 SEM Analysis
The SEM images of the five USY based catalysts are shown in Fig. 4.1. The commercial USY catalyst (Fig. 4.1a) shows flattened octahedral crystallites along with a few rod like particles typical of a faujasite crystal structure [1]. The SEM micrograph of UC0.75 shows the crystals of USY along with the presence of some spherical shaped particles of SBA-16. The spherical particles are present along with the USY crystals and there is no phase segregation. Similar morphology is observed from the SEM images of UC0.92. However, in this catalyst there are observed more spherical particles compared to UC0.75 catalyst. Comparatively the highest mesoporous spherical particles are observed in UC1.2 along with the crystalline structure of USY. This exactly corresponds to its synthesis procedure as UC1.2 is composed of the lowest USY content as compared to the other two catalysts. Uniform composite morphology is observed in US1.2 with crystalline USY particles together with some loosely aggregated morphologies that represent mesoporous SBA-15 phase.
Fig. 4.1 SEM images of the USY composite catalysts: a) Commercial USY, b) UC0.75, c) UC0.92, d) UC1.2, and e) US1.2.
4.1.2 Nitrogen Adsorption-Desorption

Nitrogen adsorption-desorption isotherms of the commercial USY and the USY composite catalysts are shown in Fig. 4.2. All the catalysts show type IV isotherm which indicates the presence of mesopores in the catalysts [2]. The commercial USY catalyst (CBV720) is dealuminated catalyst with the presence of secondary mesoporous which explain for its characteristic type IV isotherm. Lallemand [3] has also found a similar isotherm for CBV720 USY catalyst. Generally, in the lower pressure region (0.05≤\(P/P_0\)≤0.41), the adsorbed amount of \(N_2\) is observed to increase virtually linearly with change in relative pressure. This suggests monolayer adsorption of nitrogen on the pore walls [2, 4]. Nitrogen multifold adsorption in the mesopores occurred at higher relative pressures [2, 5]. It is clearly evident from these isotherms that all these catalysts have micro-mesoporous composite structure having micropores of USY present along with mesopores of SBA-16 (UC0.75, UC0.92, and UC1.2) and SBA-15 (US1.2).

\[
\text{Relative pressure (P/P_0)}
\]

\[
\text{Volume adsorbed (cm}^3\text{/g)}
\]

Fig. 4.2 \(N_2\) adsorption-desorption isotherms of the USY composite catalysts: a) Commercial USY, b) UC0.75, c) UC0.92, d) UC1.2, and e) US1.2.

The pore size distribution of the above five catalysts is shown in Fig 4.3. The commercial USY as expected shows the presence of both the micropores and the mesopores. As discussed earlier, these mesopores may result from some post synthesis procedure of zeolite Y that is required for the formation of ultra-stable Y zeolite. The pore size distribution of UC0.75 is similar to that of USY, however, it has reduced quantity of micropores to that of
USY. It has a peak with pore size of 2.8 nm in addition to the mesopores observed in the parent USY catalyst. UC0.92 also has pores of the size 3.62 nm similar to UC0.75, but it contains greater quantity of mesopores with 2.8 nm. Additionally, this catalyst also has a small peak indexed at 4.54 nm and a broad peak centered at pore size of 7.12 nm. The pore size distribution of UC0.92 and UC1.2 is almost similar with the higher pore sizes of 3.62 nm in UC1.2 and less micropores to that of UC0.92. UC1.2 and US1.2 also exhibit similar pore sizes at 3.62 nm. However, US1.2 has two additional mesoporous peaks centered at pore sizes 4.75 nm and 5.44 nm and it contains higher quantity of micropores compared to UC1.2. In all these composite catalysts, the lower pore size range is considered to be contributed by the parent USY, however, the upper range of the pore sizes are participated by the mesoporous silica. It is important to mention that as all the composite catalysts were synthesized in the acidic medium and the final gel before the hydrothermal treatment was maintained at the pH value of 3, it is therefore probable that some aluminum leaching took place and contributed towards the mesoporosity of the composite catalysts.

Fig. 4.3 Pore size distribution of the USY composite catalysts.

The structural properties of the catalysts are shown in Table 4.1 and Table 4.2. Table 4.1 shows the TEOS to parent USY ratios and the type of surface active agent used during the synthesis. As all the composite catalysts are synthesized in the acidic medium and the final gel before the hydrothermal treatment is maintained at the pH value of 3, it is expected that some aluminum leaching took place and therefore all the synthesized composites are showing higher Si/Al ratio to that of the parent USY catalyst. Moreover, the addition of TEOS, a silica
containing compound, has also contributed in increasing the Si/Al ratio of the composite catalysts. It is observed that the Si/Al ratio increases with an increase in TEOS/USY ratio. On the other hand, the N$_2$-BET surface area of the catalysts as shown in Table 4.2 is found to decrease with an increase in TEOS/USY ratio. The micropore area and micropore volume decrease with an increase in TEOS/USY ratio and BJH area and BJH volume increase with an increase in TEOS/USY ratio. It clearly indicates that increase in TEOS/USY ratio subsequently decreases the microporosity and increases the mesoporosity. The structural properties of the catalysts are clearly representing the composite nature of these catalysts.

### Table 4.1 Synthesis factors of the USY composite catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TEOS/USY</th>
<th>Surface active agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>USY</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>UC0.75</td>
<td>0.75</td>
<td>F-127</td>
</tr>
<tr>
<td>UC0.92</td>
<td>0.92</td>
<td>F-127</td>
</tr>
<tr>
<td>UC1.2</td>
<td>1.2</td>
<td>F-127</td>
</tr>
<tr>
<td>US1.2</td>
<td>1.2</td>
<td>P-123</td>
</tr>
</tbody>
</table>

### Table 4.2 Structural properties of the USY composite catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al ratio by EDX</th>
<th>$S_g$ (m$^2$/g)</th>
<th>$S_{mi}$ (m$^2$/g)</th>
<th>$BJH S_g$ (m$^2$/g)</th>
<th>$v_{mp}$ (cm$^3$/g)</th>
<th>$BJH v_p$ (cm$^3$/g)</th>
<th>$BJH d_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USY</td>
<td>17.65</td>
<td>722.2</td>
<td>585.8</td>
<td>45.09</td>
<td>0.265</td>
<td>0.0525</td>
<td>3.23</td>
</tr>
<tr>
<td>UC0.75</td>
<td>31.65</td>
<td>739.2</td>
<td>542.1</td>
<td>76.00</td>
<td>0.243</td>
<td>0.0833</td>
<td>3.55</td>
</tr>
<tr>
<td>UC0.92</td>
<td>34.76</td>
<td>620.8</td>
<td>419.5</td>
<td>82.20</td>
<td>0.189</td>
<td>0.089</td>
<td>3.54</td>
</tr>
<tr>
<td>UC1.2</td>
<td>46.95</td>
<td>593.1</td>
<td>385.1</td>
<td>85.52</td>
<td>0.172</td>
<td>0.0925</td>
<td>3.55</td>
</tr>
<tr>
<td>US1.2</td>
<td>46.27</td>
<td>603.5</td>
<td>384.2</td>
<td>90.39</td>
<td>0.175</td>
<td>0.1039</td>
<td>3.94</td>
</tr>
</tbody>
</table>

$S_g$ is surface area by using BET method, $S_{mi}$ is micropore area obtained by t-plot, $BJH S_g$ is BJH adsorption cumulative surface area of the pore between 17Å and 3000Å width, $v_{mp}$ is micropore volume obtained by t-plot, $BJH v_p$ is BJH adsorption cumulative volume of the pore between 17Å and 3000Å width, and $BJH d_p$ is BJH adsorption average pore diameter.

#### 4.1.3 Small Angle and Wide Angle XRD Analyses

The small angle X-ray diffraction patterns of all the five catalysts are displayed in Fig. 4.4. For UC1.2 there is a broad peak centered at 2 theta 0.93 that is attributed to (110) crystallographic planes reflection [6]. It indicates the presence of ordered mesopores of Im3m cubic structure in UC1.2 [6, 7] and suggests the formation of SBA-16 material in the composite catalyst. Two tiny peaks though less visible are present at 2 theta of 1.66 and 1.76 that are assigned to (200) and (211), respectively. UC0.92 and UC0.75 also show the characteristic peaks, however, the peak intensity decreases with a decrease in TEOS/USY ratio. The decrease in the peak intensity is a sign of lower order of the mesoporous structure.
The presence of USY structure has posed difficulty in the formation of ordered mesoporous assembly [8].

Fig. 4.4 Small angle XRD patterns of the USY composite catalysts: a) UC0.75, b) UC0.92, c) UC1.2, and d) US1.2.

Fig. 4.5 Wide angle XRD patterns of the USY composite catalysts: a) Commercial USY, b) UC0.75, c) UC0.92, d) UC1.2, and e) US1.2.
Wide angle XRD results of all the catalysts are shown in Fig. 4.5. The parent USY catalyst shows the characteristic diffractogram of a zeolite Y catalyst. It is observed from the diffraction pattern of the composite catalysts that the zeolite structure of all the catalysts is preserved. However, the addition of mesoporosity in the composite catalysts is found to lower the crystallinity of these catalysts as that of the parent USY. It is observed that an increase in the ratio of TEOS/USY results in the decrease of crystallinity of the composite catalysts.

4.1.4 FTIR Spectroscopy
The acidity of the catalysts is evaluated by the use of Py-FTIR technique. Py-FTIR spectra of the catalysts are displayed in Fig. 4.6. All the catalysts exhibit a characteristic band at 1445 cm\(^{-1}\). This band is weak in the case of USY and UC0.75. All the catalysts except UC0.75 and USY also have an intensified band at 1595 cm\(^{-1}\). Both these bands correspond to the presence of Lewis acid sites [9]. All the five catalysts possess another band at 1485 cm\(^{-1}\) that signifies the pyridine association with Brønsted and Lewis acid sites [9, 10]. This band is prominent in each composite catalyst and intensifies with increase in the mesoporous content. UC1.2 and USY has a broad band at 1633 cm\(^{-1}\) that attributes to the presence of Brønsted acid sites. All the four composite catalysts possess strong acid sites compared to the original USY catalyst.

The FTIR spectra of the catalysts are presented in Fig. 4.7. All the catalysts display transmission bands at 457 cm\(^{-1}\) and 829 cm\(^{-1}\) that are attributed to Si–O–Si bond vibration [11]. There is also a broad band from 1000–1237 cm\(^{-1}\) assigned to asymmetric stretching of Si–O–Si [12]. The transmission band at 1633 cm\(^{-1}\) represents the –OH group flexural vibration [13]. Another band at 3441 cm\(^{-1}\) is assigned to stretching vibration of the adsorbed water molecules and the terminal Si–OH bond [13]. All the catalysts exhibit a band at 605 cm\(^{-1}\) indicating the presence of zeolite framework containing AlO\(_4\) and SiO\(_4\) tetrahedral units [14–21].
Fig. 4.6 FTIR spectra of pyridine adsorbed USY composite catalysts: a) Commercial USY, b) UC0.75, c) UC0.92, d) UC1.2, and e) US1.2.

Fig. 4.7 FTIR spectra of the USY composite catalysts: a) Commercial USY, b) UC1.2, c) UC0.92, d) UC0.75, and e) US1.2.
4.2 Hydrocracking Performance of the Catalysts

All the catalysts discussed above were tested for their activity and selectivity in the hydrocracking reactions of the model plastic mixture. Fig. 4.8 shows the results of the hydrocracking experiments in 650 ml autoclave reactor with 20 bar initial cold hydrogen pressure, 60 min residence time, 20:1 feed to catalyst ratio (by wt.), and at three levels of reaction temperature (375°C, 400°C, and 425°C).

At the reaction temperature of 375°C, out of all the catalysts, the composite catalyst UC0.75 has the highest conversion whereas the parent USY catalyst shows the least ability to crack the model plastic mixture. All the composite catalysts, therefore, showed higher activity than the parent USY catalyst. The highest liquid selectivity is provided by UC0.75 and UC0.92 catalysts where UC0.75 delivered the highest oil (n-heptane soluble liquids) yield while the UC0.92 provided relatively lower gas yield. The composite catalyst, UC0.75, has the highest content of the USY with increased microporosity. As the diffusion limitations are less important at lower temperatures, its activity is the highest at the lower temperature and selectivity improvement is probably due to increased mesoporous portion to that of USY catalysts.

At 400°C UC1.2 managed to provide the highest activity and selectivity towards the liquid and oil products. Again the least conversion and liquid yield are obtained with the parent USY catalyst. All the other catalysts (UC0.75, UC0.92, and US1.2) virtually showed the same activity and selectivity. UC1.2 has the highest TEOS/USY ratio and therefore contains the highest mesoporous content that resulted into improved pore diffusion and shape selectivity for the larger molecules. These factors caused increased activity and increased selectivity of UC1.2 towards the liquid yield.

At the highest temperature of 425°C all the catalyst showed virtually similar performance, apart from UC1.2 which showed slightly better activity as it provided increased conversion and increased amount of gases. It seems that the effect of using different catalysts does not matter at this high temperature. Similar observation is reported by other researchers in the field. This high reaction temperature had probably produced enough thermal energy to meet the activation energy required for the reaction to take place. So the role of catalyst could only be important at lower temperatures.
Fig. 4.8 Results of the hydrocracking reactions of model plastic mixture over the USY composite catalysts. 650 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
For all the catalysts the conversion, liquid and oil yields, and the gas yield are increased with an increase in temperature. At lower temperature, the conversion and oil and liquid yields are higher for the composite catalysts containing increased micropores whereas at higher temperature, the conversion and oil and liquid yields are higher for the catalysts containing increased mesoporous content. It seems that mesoporous catalysts are more active at higher temperature and their activity increased more rapidly with temperature compared to the USY catalyst.

Gas chromatography analyses of n-heptane soluble liquids are shown in Fig. 4.9. It is observed that at the lowest temperature of 375°C, UC0.75 yields the highest gasoline fraction. However, at this temperature USY is more selective towards light diesel component among all the other catalysts. At higher temperature of 400°C, USY yields the highest gasoline fraction closely followed by UC1.2. Here, the composite catalysts are found more selective towards light diesel with UC0.75 is found to have the highest light diesel fraction. At the highest temperature of 425°C, UC0.75 produced the highest amount of gasoline among all the other catalysts.

Fig. 4.9 Results of GC analysis of the n-heptane soluble liquids obtained by the hydrocracking of model plastic mixture over the USY composite catalysts. 650 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
Additional experiments were carried out at a temperature of 400°C to observe the effect of residence time on the hydrocracking performance of the catalysts. The results of hydrocracking reactions for the model plastic mixture at three residence times, namely, 30 min, 60 min, and 90 min are shown in Fig. 4.10. It is observed that for all the catalysts, increase in residence time increases the conversion, gas yield, oil yield, and liquid yield. Moreover, generally the conversion and product yields are increased more rapidly initially, i.e., between 30 and 60 min and then increased somewhat slowly with time. This suggests that rather long time will be required for the complete conversion of the plastic mixture and still longer time will be required for the conversion of liquids to the gases, if it is ever possible with these catalysts under these conditions.

![Conversion vs Residence Time](image1.png)

![Oil Yield vs Residence Time](image2.png)

![Gas Yield vs Residence Time](image3.png)

![Liquid Yield vs Residence Time](image4.png)

Fig. 4.10 Effect of reaction time on the hydrocracking of model plastic mixture over the USY composite catalysts. 650 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 400°C reaction temperature, and 20:1 feed to catalyst ratio (by weight).

4.3 Summary

The characterization of the catalysts confirms the formation of composite structures in the catalysts. However, the presence of USY has affected the order of the mesoporous phase. It is
observed that the crystallinity of the microporous USY catalyst has been remained intact, however, the crystallinity decreased with an increase in TEOS/USY ratio.

In the hydrocracking experiments, the conversion and liquid yield for all the composite catalysts are found far better than USY catalyst which may correspond to the ease of accessibility to active sites in the composite catalysts. UC0.75 with the lowest TEOS/USY ratio is found the best catalyst at lower temperature of 375°C. As the temperature is increased UC1.2 has shown increase in the conversion and oil and liquid yields. UC1.2 is synthesized with the highest TEOS/USY ratio. This possibly due to the increased mesoporous content of UC1.2 and that the diffusion limitations are more important at high temperatures. The concentration of gasoline in UC0.75 is decreased while it is increased in UC1.2 also suggests lower activity of the UC0.75 and higher activity of UC1.2. Comparing UC1.2 and US1.2 having the same TEOS/USY ratio but different mesophase, UC1.2 generally showed better performance. It might correspond to the rather favorable diffusion in 3D cubic mesoporous arrangement in SBA-16 as compared to the diffusion in 2D array of hexagonal pores of SBA-15. At very high temperatures, the effect of the type of catalyst is not found important.

References


Chapter 5
Characterization and Hydrocracking Performance of Composites of Zeolite ZSM-5 with Mesoporous Silica

Zeolite ZSM-5 catalysts contain small micropores which may hinder the access of bulky molecules to the active centers and also promote the formation of lighter product with increased amount of gases. Composite micro-mesoporous catalysts obtained by modifying the original ZSM-5 catalyst present reduced diffusional resistances and increased activity and selectivity. In this chapter, the commercial HZSM-5 (CBV2314) catalyst and the in-house composite catalysts of the commercial HZSM-5 with mesoporous silica are characterized by various techniques and their hydrocracking performance for a model plastic mixture is studied. The catalysts are characterized using SEM analysis, nitrogen adsorption-desorption approach, small angle and wide angle XRD analyses, FTIR analysis, and Py-FTIR analysis. The catalytic activity and selectivity are evaluated at three reaction temperatures (350°C, 375°C, and 400°C) for an initial cold hydrogen pressure of 20 bar and a residence time of 60 min. The oil products obtained in the reactions are further analyzed using GC-FID.

5.1 Catalyst Characterization
5.1.1 SEM Analysis
The surface morphology of each of the catalysts is given by the SEM images shown in Fig. 5.1. The commercial HZSM-5 catalyst (CBV2314) shows small cubic shaped crystals that represent the characteristic HZSM-5 structure [1, 2]. The SEM micrographs of ZC-P display cubic HZSM-5 crystals present uniformly with the fibrous transparent worm like structures that are the characteristic feature of an SBA-15 [3]. The SEM images of ZC-F show the presence of cubic crystals of ZSM-5 along with some spherical shaped particles that represent the presence of SBA-16 mesoporous content as it is synthesized with F-127 as the surface directing agent. There is no phase segregation that represents the presence of uniform composite structure. For the ZC-FP, the SEM micrographs show the presence of cubic crystals of HZSM-5 along with the spherical particles of SBA-16 together with transparent loose aggregates of SBA-15. The catalyst displays the co-existence of cubic and hexagonal mesoporous phase along with microporous crystals of HZSM-5. The overall morphology of the composite catalysts is highly coarse compared to the HZSM-5 catalyst.
Fig. 5.1 SEM images of the HZSM-5 composite catalysts: (a and b) HZSM-5, (c and d) ZC-P, (e and f) ZC-FP, and (g and h) ZC-F.
The desilication process used in the synthesis of the composite catalysts resulted in the formation of coarse texture in these composites [4].

### 5.1.2 Nitrogen Adsorption-Desorption

Nitrogen adsorption-desorption isotherms of the four catalysts are displayed in Fig. 5.2. The isotherm of HZSM-5 displays type I isotherm that is a characteristic isotherm of the microporous zeolite materials [5]. In the area of lower relative pressure, the isotherms of ZC-F, ZC-FP, and ZC-P show a linear increase in adsorbed amount with an increase in relative pressure. This shows monolayer adsorption of N₂ on the pore walls [6]. However, there is observed a steep increase in the area of higher relative pressure from 0.67–0.90 in the adsorption branch of the isotherms. It represents filling up of the mesopores by the adsorbed nitrogen and multifold adsorption in the mesopores of the catalysts is the result. All the composite catalysts are representing type IV isotherm with characteristic H2 hysteresis. The isotherms of ZC-F, ZC-FP, and ZC-P catalysts clearly display the presence of micro-mesoporous composite assembly, i.e., having micropores of HZSM-5 present along with mesoporous silica.

The pore size distribution of all the catalysts is presented in Fig. 5.3. It is clearly evident from the figure that the pore size distribution of ZC-F and ZC-FP resembles each other like their isotherms. It might be attributed to the fact that ZC-FP mesoporous portion is dominated by the cubic Im3m space group symmetry introduced by F-127 as compared to hexagonal P6mm plane group symmetry added by P-123. Both ZC-F and ZC-FP have broad pore size
distribution centered at about 7.45 nm with two smaller peaks at 3.62 nm and 4.34 nm. However, ZC-F has slightly more quantity of mesopores and somewhat reduced amount of micropores compared to ZC-FP. ZC-P has the bi-modal pore sizes with an intense peak at 5.69 nm and a smaller one at 3.03 nm. It is apparent that all the composite catalysts have increased quantity of mesopores compared to the parent HZSM-5 resulting due to the desilication of HZSM-5 and the formation of the mesostructure in the presence of surface active agents used in their synthesis.

Fig. 5.2 N₂ adsorption-desorption isotherms of the HZSM-5 composite catalysts: a) HZSM-5, b) ZC-F, c) ZC-FP, and d) ZC-P.

Fig. 5.3 Pore size distribution of the HZSM composite catalysts.
The structural properties of catalysts are shown in Tables 5.1. It is found that the surface areas of all the composite catalysts are higher as compared to the HZSM-5 catalyst with the highest in the case of ZC-P. The highest mesoporous area is present in ZC-F.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al ratio by EDX</th>
<th>$S_g$ (m$^2$/g)</th>
<th>$S_{mi}$ (m$^2$/g)</th>
<th>$BJH S_g$ (m$^2$/g)</th>
<th>$v_{mp}$ (cm$^3$/g)</th>
<th>$BJH v_p$ (cm$^3$/g)</th>
<th>$BJH d_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>13.56</td>
<td>339.2</td>
<td>283.5</td>
<td>20.66</td>
<td>0.127</td>
<td>0.023</td>
<td>3.24</td>
</tr>
<tr>
<td>ZC-F</td>
<td>34.56</td>
<td>364.2</td>
<td>162.6</td>
<td>95.05</td>
<td>0.068</td>
<td>0.12</td>
<td>6.52</td>
</tr>
<tr>
<td>ZC-FP</td>
<td>33.98</td>
<td>370.8</td>
<td>184.3</td>
<td>84.67</td>
<td>0.078</td>
<td>0.10</td>
<td>6.53</td>
</tr>
<tr>
<td>ZC-P</td>
<td>31.21</td>
<td>382.5</td>
<td>208.4</td>
<td>83.45</td>
<td>0.094</td>
<td>0.19</td>
<td>6.65</td>
</tr>
</tbody>
</table>

$S_g$ is surface area by using BET method, $S_{mi}$ is micropore area obtained by $t$-plot, $BJH S_g$ is $BJH$ adsorption cumulative surface area of the pore between 17Å and 3000Å width, $v_{mp}$ is micropore volume obtained by $t$-plot, $BJH v_p$ is $BJH$ adsorption cumulative volume of the pore between 17Å and 3000Å width, and $BJH d_p$ is $BJH$ adsorption average pore diameter.

### 5.1.3 Small Angle and Wide Angle XRD Analyses

The small angle X-ray diffraction patterns of the catalysts are shown in Fig. 5.4. ZC-P catalyst displays three well resolved peaks at 20 value of 0.97, 1.64, and 1.88 that are attributed to (100), (110), and (200) reflections, respectively [3, 7]. Well-ordered hexagonal mesoporous structure with P6mm symmetry is found in this composite catalyst. X-ray diffraction pattern of ZC-F presents three peaks at 20 value of 0.73, 1.11, and 1.23 that indicate (110), (200), and (211) planes, respectively [8, 9]. Ordered cubic Im3m mesostructure is therefore formed in this composite catalyst. The catalyst ZC-FP displays a sharp peak at 20 value of 0.68 with a shoulder peak at 0.74 assigned to (100) and (110) reflections, respectively [3, 7‒9]. Comparatively less ordered structure is found in ZC-FP. This might be attributed to the co-existence of cubic and hexagonal mesostructures in the same catalyst.

Wide angle XRD patterns of all the four catalysts are shown in Fig. 5.5. HZSM-5 shows well resolved sharp peaks that show highly crystalline structure of HZSM-5. The diffractograms of the composite catalysts show that the crystallinity of the HZSM-5 is retained after the alkaline treatment. However, with the introduction of mesoporosity there is observed a decrease in crystallinity in the composite catalysts. Among the composite catalysts, the crystalline behavior of ZC-P is observed to be the closest to the parent HZSM-5 catalyst.
5.1.4 FTIR Spectroscopy

Pyridine FTIR spectrum, Fig 5.6, for each of the catalysts displays a significant band at 1540 cm\(^{-1}\) assigned to Brønsted acid site [10, 11]. The band is relatively weak for ZC-P and strong for ZC-F. There is another band at 1640 cm\(^{-1}\) corresponds to Bronsted acid site [11, 12] applicable only to HZSM-5 and ZC-FP. For all the catalysts except ZC-FP, two additional
bands are observed at 1456 cm\(^{-1}\) and 1623 cm\(^{-1}\). Both of these bands are attributed to the pyridine association with Lewis acid sites [12, 13]. All the mesoporous composite catalysts are found to exhibit more acid sites as compared to the parent HZSM-5 catalyst.

The FTIR spectra, Fig. 5.7, of all the composite catalysts along with the HZSM-5 catalyst show a transmission band at 546 cm\(^{-1}\) that is attributed to the asymmetrical stretching vibration of double-five ring of ZSM-5 [14]. This band along with the band at 463 cm\(^{-1}\) confirms the presence of typical MFI structure in HZSM-5 and all the composite catalysts [15, 16]. Each catalyst displays a band at 3652 cm\(^{-1}\) that is assigned to the terminal Si–OH bond stretching vibration and adsorbed water molecules [14]. Another band at 1634 cm\(^{-1}\) is existed in all the catalysts that corresponds to the flexural vibration of –OH bond [14]. Each composite catalyst and HZSM-5 catalyst exhibit a band at 463 cm\(^{-1}\) that indicates the bending mode of tetrahedral Si–O. The catalysts also possess a broad peak centered at 1087 cm\(^{-1}\) and a shoulder of that peak at 1224 cm\(^{-1}\) that are assigned to asymmetrical vibration of T–O–T bond [14]. Another band at 795 cm\(^{-1}\) is attributed to symmetric stretching of T–O–T bond [14].

![FTIR spectra of the pyridine adsorbed HZSM-5 composite catalysts](image)

**Fig. 5.6 FTIR spectra of the pyridine adsorbed HZSM-5 composite catalysts:** a) HZSM-5, b) ZC-P, c) ZC-FP, and d) ZC-F.
Fig. 5.7 FTIR spectra of the HZSM-5 composite catalysts: (a) HZSM-5, (b) ZC-P, (c) ZC-F, and (d) ZC-FP.

5.2 Hydrocracking Performance of the Catalysts

Fig. 5.8 shows the results of the catalytic hydrocracking experiments over HZSM-5 composite catalysts in 500 ml autoclave reactor and at three levels of temperature. At the reaction temperature of 350°C, all the composite catalysts produced higher conversion and yield of the liquid products to that of the parent HZSM-5 catalyst. The HZSM-5 catalyst delivered the highest gas yield. The reason for these observations may be attributed to the improved diffusion of the large polymeric molecules to the active sites due to the presence of mesopores in the composite catalysts. The mesopores also allowed the larger liquid molecules formed to diffuse out of the catalyst pores without further cracking to cause higher yield of the liquid product in the composite catalysts. The small micropores in HZSM-5 hindered the diffusion of large liquid molecules, therefore, the large molecules were cracked and cracked into smaller molecules and hence the HZSM-5 catalysts yielded increased amount of gaseous content. Among the composite catalysts, ZC-P with the highest microporous area as compared to the other composite catalysts yielded the highest conversion and considerable amount of gaseous product whereas the highest liquid yield and the least gaseous product were obtained over ZC-FP. ZC-FP catalyst has the combination of both the hexagonal and cubic pore arrangement. The combination might have improved the diffusion for large molecular weight product.
Fig. 5.8 Results of the hydrocracking of model plastic mixture over the HZSM-5 composite catalysts. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
At 375°C again all the composite catalysts provided increased conversion and liquid selectivity but decreased amount of gaseous products compared to the parent HZSM-5 catalyst. Both ZC-P and ZC-FP offered virtually the same conversion but ZC-FP provided greater selectivity of liquid products and fewer amounts of gases. The increased micropore volume of ZC-P might be the cause of its increased gas yield and decreased liquid selectivity.

At the highest temperature of 400°C all the catalysts came up with same activity performance giving virtually similar conversion. It might be happened due to increased thermal energy provided at this temperature. Again, ZC-FP catalyst provided the highest liquid yield and the lowest gas selectivity contrary to the HZSM-5 catalyst which delivered the lowest liquid yield and the highest gas selectivity. Microporous cavities in HZSM-5 resulted in the highest gas yield and the lowest liquid yield in HZSM-5 whereas the highest liquid yield and the lowest gas yield offered by ZC-FP was due to its improved diffusion characteristics.

The gas chromatography analyses of the n-heptane soluble liquids are shown in Fig. 5.9. At 350°C the highest amount of gasoline is obtained from HZSM-5 catalyst. The shape selectivity of HZSM-5 allowed to produce lighter liquid in greater amount. The light diesel and heavy diesel products underwent cracking in order to leave the small pores of the catalyst. Among the composite catalysts, ZC-P produced the highest gasoline closely followed by ZC-FP. ZC-P contains the highest micropore volume which may be the reason for its increased gasoline content. ZC-FP and ZC-F are more selective towards diesel fractions. ZC-FP produced the highest amount of light diesel while ZC-F produced the highest amount of heavy diesel. At 375°C both ZC-FP and HZSM-5 catalysts are found highly selective towards gasoline. ZC-FP produced gasoline at the expense of light diesel. The light diesel fraction of ZC-FP at higher temperature underwent further cracking to produce gasoline fraction. At this temperature the least amount of gasoline and the highest fraction of diesels are produced by ZC-P catalyst. Again at 400°C HZSM-5 and ZC-FP are found highly selective towards gasoline where the light and heavy diesel fractions of ZC-FP are contributing to the increased gasoline concentration in the product. With ZC-P when compared to the results at 375°C, at this temperature, both the gasoline and light diesel fractions are increased with a decrease in heavy diesel fraction.
Fig. 5.9 Results of GC analysis of the n-heptane soluble liquids obtained by the hydrocracking of model plastic mixture over the HZSM-5 composite catalysts. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
5.3 Summary

Three in-house composite catalysts of HZSM-5 with mesoporous silica, synthesized using three different surface directing agents are well characterized and tested for the hydrocracking of a model plastic mixture. The characterization of the catalysts has confirmed the formation of the composites of HZSM-5 with mesoporous silica. ZC-P catalyst is formed with highly ordered structure whereas comparatively less ordered structure is present in ZC-FP. This might be due to the presence of two types of mesostructures in ZC-FP catalyst. During the synthesis the composite catalysts maintained the microporous crystallinity of HZSM-5. However, the mesoporous character has decreased the intensity of crystallinity. ZC-P catalyst has shown rather closer crystallinity to the HZSM-5 catalyst.

In the hydrocracking testing of the catalysts, ZC-FP catalyst is found the best catalyst as it provided very high conversions and yielded the highest quantity of liquid product with the lowest gaseous components at all reaction temperatures. Although, ZC-P is found more active at lower temperature of 350°C than ZC-FP but ZC-FP has delivered greater liquid yield even its conversion is lower at that temperature. The n-heptane solubles show both HZSM-5 and ZC-FP contain high content of gasoline fraction. However, HZSM-5 due to its microporous nature is found highly selective towards gaseous product.

References


Chapter 6
Characterization and Hydrocracking Performance of Composites of Zeolite Beta with Mesoporous Silica

The dimensions of the pores in microporous zeolite catalysts such as zeolite beta are small that may create the problem of diffusion of heavy molecules to the active centers. Also, they inhibit the formation of relatively large molecular weight liquid products and contribute to the formation of lighter gaseous products. Composite micro-mesoporous catalysts not only decrease the diffusional resistances but they can also provide superior activity and preferred liquid selectivity. In this chapter, the commercial zeolite beta (CP811C300) catalyst and the in-house composite catalysts of the commercial catalyst with mesoporous silica are characterized by various techniques and their hydrocracking performance for a model plastic mixture is studied. The catalysts are characterized using SEM analysis, nitrogen adsorption-desorption approach, small angle and wide angle XRD analyses, FTIR analysis, and Py-FTIR analysis. The catalytic activity and selectivity are evaluated at three reaction temperatures (350°C, 375°C, and 400°C) for an initial cold hydrogen pressure of 20 bar and a residence time of 60 min. The n-heptane soluble liquid products (oils) obtained in the hydrocracking reactions are further analyzed by applying GC-FID.

6.1 Catalyst Characterization
6.1.1 SEM Analysis

The SEM micrographs of the catalysts are displayed in Fig. 6.1. The image of the commercial beta zeolite (B300) shows ball like distinct particles that display characteristic crystals of zeolite beta [1, 2]. The morphology of the Al impregnated zeolite beta (BAl) is similar to that of zeolite beta. However, in this catalyst some partial agglomeration is observed due to aluminum impregnation. BC11.1 catalyst shows only a few discrete particles of zeolite beta along with large rough surface agglomerates with irregular shaped morphologies. These rough large agglomerates represent amorphous mesoporous portion. As this catalyst is prepared by desilication of zeolite beta with 1.5 M NaOH solution, it seems that desilication has resulted in the destruction of the parent zeolite beta structure. The micrograph of BC5.7 catalyst displays morphology similar to that of BC11.1 catalyst. However, in this catalyst there are present more regular shaped zeolite beta particles to that of BC11.1. This can be explained on the basis of using lower TEOS/beta ratio in the preparation of BC5.7. The morphology of BC0.7 shows higher content of individual crystals of zeolite beta. This
catalyst is desilicated with lower molarity of NaOH solution as compared to BC11.1. The lower molarity of NaOH resulted in the formation of less distorted structures of zeolite beta. Along with zeolite beta particles there are irregularly shaped aggregates that represent amorphous mesoporous phase. Regular shaped discrete zeolite beta crystals are shown by BC27 (Fig. 6.1f). As this catalyst is prepared in 0 M NaOH solution and there is no desilication, hence no destruction of the zeolite structure. Also, there are some irregularly shaped masses that represent mesoporous content. Compared to BC27, BC48 shows increased aggregated structures and higher mesoporous silica. Higher hydrothermal treatment time to BC48 has seemed to increase the mesoporous portion to a considerable extent.

![Fig. 6.1 SEM images of the zeolite beta composite catalysts: a) B300, b) BA1, c) BC11.1, d) BC5.7, e) BC0.7, f) BC27, and g and h) BC48.](image-url)
6.1.2 Nitrogen Adsorption-Desorption

Fig. 6.2 shows nitrogen adsorption-desorption isotherms of the catalysts. The commercial zeolite beta and the aluminum impregnated zeolite beta catalysts display type I isotherm, that is a characteristic isotherm of the microporous zeolitic materials [3]. The isotherms of all the other beta modified catalysts such as BC11.1, BC5.7, BC0.7, BC27, and BC48 are similar to that of the parent beta catalyst in the region of lower relative pressure. All these catalysts are showing type IV isotherm with characteristic H2 hysteresis loop [4]. The nature of the
isotherms demonstrates the formation of the composite assembly [5] of these catalysts having micropores of zeolite beta present along side mesoporous silica.

![N2 adsorption-desorption isotherms](image)

Fig. 6.2 N₂ adsorption-desorption isotherms of the zeolite beta composite catalysts: (a) B300, (b) BAl, (c) BC27, (d) BC48, (e) BC0.7, (f) BC11.1, and (g) BC5.7.

The pore size distribution of the catalysts is depicted in Fig. 6.3. It is found that the aluminum impregnated zeolite beta catalyst (BAl) has reduced amount of micropores than that of B300. The aluminum impregnation has caused to occupy some spaces in the micropores of the zeolite beta and therefore resulted in a decrease in the microporous volume. It is observed that BC11.1 catalyst is characterized by broad pore size distribution with most of the pore sizes of 3.62 nm, 4.15 nm, and 4.75 nm. On the other hand, BC5.7 and BC0.7 catalysts show bimodal pore size distribution. The former with lower TEOS/beta ratio has a sharp peak indexed at 3.62 nm and a small peak at 5.1 nm whereas for the latter most of the pore sizes are of 5.43 nm with a smaller peak indexed at 3.62 nm. BC27 has majority of pore sizes of 3.63 nm and a few of 2.8 nm. With decrease in molarity of NaOH solution there is a trend towards more uniform pore size with bimodal pore size distributions. The catalyst with 0 M NaOH solution (BC27) has the highest content of micropores along with the mesopores as compared to the other composite catalysts. In the desilicated composite catalysts, however, the parent zeolite beta has also developed some mesopores due to the surface defects created by the extraction of silica from the structure. BC48 has a narrow pore size distribution with a sharp peak indexed at 3.65 nm and two smaller peaks at 2.65 nm and 5.19 nm. The pore size
distribution of BC27 and BC48 are similar and both the catalysts have nearly the same distribution around 2.65 nm and 3.65 nm. However, in the case of BC27 there is an increased amount of micropores whereas BC48 has significant quantity of mesopores. It is therefore revealed that an increase in hydrothermal treatment time has resulted in decrease of micropore quantity and an increase in the amount of mesopores with larger pore size.

Fig. 6.3 Pore size distribution of the zeolite beat composite catalysts.

The structural properties of the catalysts from nitrogen physisorption are shown in Table 6.1. The highest surface area is found in BC27 that is followed by BC48. Both of these catalysts
are composite catalysts of zeolite beta without any desilication treatment. The surface area of all the desilicated catalysts (BC11.1, BC5.7, and BC0.7) is lower than that of the parent beta catalyst. Among the composite catalysts the highest micropore volume is displayed by BC27 followed by BC48. All these results strengthen the fact that the structure of zeolite beta in desilicated composites is distorted, whereas, in BC27 and BC48 the structure of zeolite beta remains intact in the final composite catalyst. Therefore zeolite beta along with the mesoporous silica coherently contributed towards increase in the surface area of these catalysts. The highest BJH pore volume is found in BC48. This catalyst has found to contain the highest mesoporous content confirmed also by the other characterization techniques.

### Table 6.1 Structural properties of the zeolite beta composite catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( S_p ) (m(^2)/g)</th>
<th>( S_{mi} ) (m(^2)/g)</th>
<th>( BJH S_t ) (m(^2)/g)</th>
<th>( v_{mp} ) (cm(^3)/g)</th>
<th>( BJH v_p ) (cm(^3)/g)</th>
<th>( BJH d_p ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B300</td>
<td>581.9</td>
<td>465.4</td>
<td>43.44</td>
<td>0.210</td>
<td>0.0465</td>
<td>3.23</td>
</tr>
<tr>
<td>BA1</td>
<td>499.5</td>
<td>430.9</td>
<td>41.89</td>
<td>0.198</td>
<td>0.045</td>
<td>3.24</td>
</tr>
<tr>
<td>BC11.1</td>
<td>408.40</td>
<td>43.01</td>
<td>165.4</td>
<td>0.0105</td>
<td>0.1999</td>
<td>6.49</td>
</tr>
<tr>
<td>BC5.7</td>
<td>475.5</td>
<td>51.79</td>
<td>192.2</td>
<td>0.01104</td>
<td>0.2389</td>
<td>6.50</td>
</tr>
<tr>
<td>BC0.7</td>
<td>399.1</td>
<td>11.35</td>
<td>185.5</td>
<td>0.00453</td>
<td>0.222</td>
<td>6.50</td>
</tr>
<tr>
<td>BC27</td>
<td>775.4</td>
<td>309.1</td>
<td>180.7</td>
<td>0.123</td>
<td>0.207</td>
<td>6.40</td>
</tr>
<tr>
<td>BC48</td>
<td>719.2</td>
<td>229.1</td>
<td>198.1</td>
<td>0.0856</td>
<td>0.249</td>
<td>6.48</td>
</tr>
</tbody>
</table>

\( S_p \) is surface area by using BET method, \( S_{mi} \) is micropore area obtained by t-plot, \( BJH S_t \) is BJH adsorption cumulative surface area of the pore between 17Å and 3000Å width, \( v_{mp} \) is micropore volume obtained by t-plot, \( BJH v_p \) is BJH adsorption cumulative volume of the pore between 17Å and 3000Å width, and \( BJH d_p \) is BJH adsorption average pore diameter.

#### 6.1.3 Small Angle and Wide Angle XRD Analyses

Fig 6.4 displays small angle X-ray diffraction patterns of the catalysts. Nearly all the composite catalysts exhibit a well resolved peak at 20 value of around 0.78 (0.88 in case of BC0.7) that corresponds to (100) reflection. Small peaks are present in all the catalysts at 20 value of around 0.98, 1.55, and 1.77 (relatively strong in BC27 and BC48 and weak in the other catalysts) that correspond to (110), (200), and (211) reflections, respectively. However, the latter peaks are not well resolved and rather weak. All catalysts possess many small peaks at 20 value of 1.16–2.8. It indicates the presence of mesostructure with low order that might be attributed to higher pH of the hydrogel mixture before the hydrothermal treatment in the synthesis step. The pH of the mixture was maintained to a value of 4 before the hydrothermal treatment to prevent the chances of aluminum leaching. Low order structure could also be resulted from the co-existence of cubic and hexagonal mesostructures in the catalysts.
The wide angle X-ray diffractogram of commercial zeolite beta shown in Fig. 6.5 presents well resolved peaks that are characteristic features of a highly crystalline zeolite beta. The diffraction pattern of BAl is shifted to slightly lower 2θ values as that of the parent zeolite beta. This has been resulted due to the impregnation of aluminum in BAl catalyst as the Si–O bond is shorter compared to Al–O bond [3]. The diffractograms of the composite catalysts with desilication treatment (BC11.1, BC5.7, and BC0.7) indicate the destruction of highly crystalline structure of zeolite beta in these composites. As a result, these catalysts are showing the diffraction pattern similar to that of an amorphous catalyst. The zeolite beta structure is found to collapse significantly by desilication and the resulting diffraction patterns of these catalysts are contributed by the mesoporous silica content. On the other hand, the introduction of the mesoporosity without desilication is found to decrease the crystallinity only without destroying the crystal structure of the zeolite beta. Among all the composite catalysts BC27 is found to be the most crystalline. Increasing time of hydrothermal treatment results in lowering of the crystalline structure of BC48 compared to BC27 indicating the presence of better mesostructure in BC48. This fact is also confirmed by SEM and nitrogen physisorption results.
Fig. 6.5 Wide angle X-ray diffraction patterns of the zeolite beta catalysts: (a) B300, (b) BAI, (c) BC27, (d) BC48, (e) BC5.7, (f) BC11.1, and (g) BC0.7.

6.1.4 FTIR Spectroscopy

Fig. 6.6 represents the Py-FTIR spectra of the catalysts. All the catalysts except BAI and BC0.7, show an intensified band at 1628 cm$^{-1}$ that corresponds to pyridine association with strong Lewis acid sites [6, 7]. Aluminum post synthesis impregnation in BAI is found to shift the band at 1628 cm$^{-1}$ in zeolite beta to a lower value of 1616 cm$^{-1}$ that also corresponds to the presence of Lewis sites. BC11.1, BC48, and BC27 display less intensified bands at 1545 cm$^{-1}$ and 1485 cm$^{-1}$ that indicate the presence of Brønsted acid sites [7] and Lewis+Bronsted acid sites, respectively [8, 9]. B300, BAI, and BC0.7 catalysts are found to contain a band at about 1540 cm$^{-1}$ assigned to Brønsted acid sites [7]. BC0.7 is found to contain the lowest amount of acid sites. Out of all the catalysts, mesoporous composites BC48 and BC27 are found to have the highest amount of acid sites more than B300 and BAI.

The FTIR spectra of the catalysts representing the atomic level connections of the chemical bonds in the catalysts are shown in Fig. 6.7. There is observed a transmission band at 557 cm$^{-1}$ exists in B300, BAI, BC48, and BC27 that corresponds to the vibrational mode of a typical zeolite beta structure having 5 or 6 membered rings of T–O–T in zeolites [2]. This band is almost absent in the other catalysts that is resulted from the desilication using NaOH solution that is seemed to destroy the zeolite beta crystalline structure to some extent. All the catalysts exhibit the transmission bands at 464 cm$^{-1}$ and 1045 cm$^{-1}$ that are attributed to T–O
bond stretching vibration and bending vibration, respectively [10]. Another significant band is observed in all the catalysts at 800 cm\(^{-1}\) that corresponds to T–O–T bond symmetric stretching [11]. The band at 950 cm\(^{-1}\) is assigned to the stretching vibration of Si–OH [12, 13]. There is found a broad peak in all the catalysts from 1034–1250 cm\(^{-1}\) that is assigned to the asymmetric stretching of Si–O–Si bond [14]. All the catalysts exhibit a broad band at 3677 cm\(^{-1}\). This band is attributed to bond vibration of the terminal silanol group [8]. Another significant band is also observed at 1663 cm\(^{-1}\) that indicates –OH bond flexural vibration [11].

Fig. 6.6 FTIR spectra of pyridine adsorbed zeolite beta composite catalysts: a) B300, b) BA1, c) BC0.7, d) BC27, e) BC5.7, f) BC11.1, and g) BC48.
6.2 Hydrocracking Performance of the Catalysts

The hydrocracking performance of the catalysts for model plastic mixture is tested at three different temperatures (360°C, 375°C, and 400°C) in a 500 ml high pressure autoclave reactor. At the reaction temperature of 360°C BC48 catalyst delivered the highest conversion with highest liquid and oil yields. The performance of this catalyst is relatively closely followed by BC27 compared to the other catalysts. Both of these catalysts have shown much better activity and selectivity towards liquids than all the other catalysts and both of these were synthesized without desilication but with improved mesoporous content. All the other catalysts performed poorly with respect to activity and desired selectivity. Increase in the hydrothermal treatment time resulted in higher mesoporous area of BC48 than that of BC27. Therefore, it facilitated improved diffusion of the initially cracked higher molecular weight polymeric molecules and the cracked liquid products through the pores of the catalysts. An enhanced activity and desired selectivity of this catalyst over the other catalysts was therefore resulted.
Fig. 6.8 Results of the hydrocracking of model plastic mixture over the zeolite beta composite catalysts. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
At 375°C again the same two catalysts BC27 and BC48 showed the increased conversion and liquid yield. However, at this temperature B300 and BAl closely followed the performance of the above two catalysts. But, both of these catalysts produced the highest gas yields. This is because both of these catalysts have dominantly microporous character which facilitated the increased gas yield. Introduction of mesoporosity in the composite catalysts resulted in the decrease of gaseous products. It is observed that the activity and liquid selectivity of the desilicated catalysts are still dissatisfactory. This last result might be attributed to the structural damage in the desilicated catalysts which is also evident from catalyst characterization results. Therefore, the performance of these desilicated catalysts might be related only to the mesoporous content of these catalysts.

At the reaction temperature of 400°C, the parent zeolite beta (B300), BAl, BC27, and BC48 have shown similar activities. However, BC27 and BC48 catalysts once again produced the highest amount of liquids whereas B300 and BAl produced higher gas yields. Moreover, the desilicated catalysts continued their poor performance with respect to both activity and liquid selectivity.

The results of gas chromatography analysis of all the catalysts at three reaction temperatures are shown in Fig. 6.8. It is found that at each temperature the catalyst B300 showed increased selectivity for the gasoline product. It corresponds to the micropores present in this catalyst that allowed low molecular weight molecules of gasoline to leave in the gas phase relatively easily. However, the gasoline component of BAl is lower than that of B300 catalyst at all the temperatures. Instead, it produces higher amount of light diesel and heavy diesel as that of the parent beta catalyst. This might be due to decrease in the micropore volume caused by the Al impregnation within the pores of beta catalyst. The BC27 and BC48 catalysts also produced increased gasoline content. Gasoline fraction of these two catalysts is close to B300 at the higher reaction temperatures of 375°C and 400°C. With increase in reaction temperature the light diesel component of BC27 and the heavy diesel component of BC48 are converted into gasoline. Increase in reaction temperature might have resulted in the breakdown of heavy molecular chains of light and heavy diesel components. Generally, all the desilicated catalysts produced much lower gasoline fraction but greater diesel fractions than that of B300, BC27, and BC48.
Fig. 8.11 Results of GC analysis of the n-heptane soluble liquids obtained by the hydrocracking of model plastic mixture over the zeolite beta composite catalysts. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, 20:1 feed to catalyst ratio (by weight).
6.3 Summary
Various in-house composite catalysts of commercial zeolite beta (CP811C-300) with mesoporous silica are characterized and subjected to hydrocracking of a model plastic mixture. The composite catalysts were synthesized with different TEOS/beta ratio, varying alkali molarity used for the desilication of the parent zeolite, and different crystallization time (hydrothermal treatment in autoclave). The parent zeolite and 5wt% Al over zeolite beta catalysts were also characterized and tested. The results of catalyst characterization showed that the crystalline structure of zeolite beta has been significantly destroyed by the desilication process. However, the composite catalysts without desilication treatment exhibit the crystalline structure of zeolite beta. The performance of these desilicated catalysts (BC11.1, BC5.7, and BC0.7) is found inferior to even zeolite beta and BAl in terms of conversion and liquid yield. Out of all the catalysts BC48 and BC27 performed better with significantly greater liquid yield, reduced gas yield, and higher conversion than that of the parent zeolite beta and all the other catalysts. GC analyses of the n-heptane solubles also demonstrate enhanced selectivity of these catalysts towards gasoline.

References


Chapter 7
Characterization and Hydrocracking Performance of Mesoporous Catalysts and Mesoporous Catalysts with Zeolite Nanoseeds

The cracking ability of silica materials is low which can be enhanced by introducing aluminum into the siliceous structure. In this chapter, two types of in-house aluminum-modified mesoporous silica catalysts are studied. Al-SBA-15, Al-SBA-16, and mesoporous materials with zeolite nanoseeds are characterized by various techniques and their hydrocracking performance for a model plastic mixture is studied. The catalysts are characterized using SEM analysis, nitrogen adsorption-desorption approach, small angle and wide angle XRD analyses, transmission electron microscopy (TEM), FTIR analysis, and Py-FTIR analysis. The catalytic activity and selectivity are evaluated at three reaction temperatures (375°C, 400°C, and 425°C) for an initial cold hydrogen pressure of 20 bar and a residence time of 60 min. The oil products obtained in the reactions are further investigated by FTIR analysis.

7.1 Catalyst Characterization
7.1.1 SEM Analysis
Fig. 7.1 shows the SEM micrograph of the aluminum-modified mesoporous catalysts. Fig. 7.1a is a representative SEM image of Al-SBA-16(10) consisting of mesoporous SBA-16 with Si/Al ratio of 10. The image shows some small randomly shaped particles on the surface of irregular shaped aggregated particles as observed by the other researchers [1]. The surface is rough with marble like texture which seems to exhibit amorphous mesoporous phase. For Al-SBA-16(20) having Si/Al ratio of 20 (Fig. 7.1b) the surface of the catalyst seems irregular. Aggregated spherical particles of small size could be seen along with the presence of some macrospheres. The loose aggregates of spherical particles may indicate the presence of mesoporous phase [2]. However, macrospheres are formed due to the higher silica content [1] in Al-SBA-16(20) as compared to Al-SBA16(10). Fig. 7.1c is the SEM image for Al-SBA-16(40) containing mesoporous SBA-16 with Si/Al ratio of 40. The image shows the presence of mostly spherical shaped particles.
Fig. 7.1 SEM images of the Al-modified mesoporous catalysts: (a) Al-SBA-16(10), (b) Al-SBA-16(20), (c) Al-SBA-16(40), (d) Al-SBA-16(10)3, (e) Al-SBA-15, (f) MZ-16, (g) MZ-15, and (h) MZ-41.
It is observed that with increase in the Si/Al ratio the morphology of the mesoporous material has formulated into more regular shaped particles whereas an increase in the quantity of aluminum results in irregularity of the particle shape and morphology. Fig. 7.1d shows the SEM image of Al-SBA-16(10)3 with Si/Al ratio of 10 prepared with pH of the gel mixture maintained at 3 instead of 7 (for all the other catalysts the pH of the gel was maintained at 7). The morphology of this material shows irregular polyhedrons. This structure was expected in the acidic medium with aluminum in the catalyst [3]. Appearance of this catalyst is similar to that of Al-SBA-16(10), however, it is observed that decrease in the pH results in the formation of comparatively smaller aggregated particles.

Fig. 7.1e is the SEM image of Al-SBA-15 catalyst. The mesoporous nature of the catalyst is evident from the micrograph. The transparent worm like fibrous structures are present which are typical of SBA-15 as reported by the other researchers in the field [4]. The SEM micrograph of MZ-16, Fig. 7.1f, displays uniform spherical particle geometries interconnected with macrospheres. Composite nature is evident as the morphology appears to display amorphous mesoporous phase. The small cubic particles represent the presence of zeolite structure. Fig. 7.1g shows the SEM image of MZ-15 which is a composite of SBA-15 mesoporous phase along with zeolitic nanoseeds. Comparing Fig. 7.1e (Al-SBA-15), it can be said that mesostructure is formed along with small aggregated zeolitic particles therefore confirming the presence of a composite catalyst. Fig. 7.1h is the representative SEM image of MZ-41. The image shows some loose aggregates along with some spherical as well as cubical particles. The loose aggregates found may indicate the presence of mesoporous MCM-41.
phase. The cubic particles seen, may demonstrate the presence of ordered zeolite structure. It is observed by the images that the cubic particles are interconnected with the mesoporous amorphous aggregates, thus strongly support the concept of composite mesoporous catalyst having zeolite nanoseeds.

Table 7.1 shows the Si/Al ratio of the synthesis gel and the actual Si/Al ratio of the catalysts as obtained from EDX analysis. It is found that the Si/Al ratios for all the catalysts except Al-SBA-16(10)3, obtained from the EDX analysis are nearly the same as that of the gel. This could be attributed to their formation in neutral medium that inhibited the possible aluminum leaching. However, Al-SBA-16(10)3 was prepared in acidic medium (pH of 3) that triggered aluminum leaching in this catalyst and the resulting catalyst was synthesized with higher Si/Al ratio. Not shown here but an Al-SBA-15 catalyst was also prepared at an extremely low pH (close to zero) which resulted in virtually complete removal of aluminum and the formation of a siliceous material.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al (gel)</th>
<th>Si/Al (EDX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-SBA-16(10)</td>
<td>10</td>
<td>10.84</td>
</tr>
<tr>
<td>Al-SBA-16(20)</td>
<td>20</td>
<td>19.52</td>
</tr>
<tr>
<td>Al-SBA-16(40)</td>
<td>40</td>
<td>40.41</td>
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<tr>
<td>Al-SBA-16(10)3</td>
<td>10</td>
<td>21.99</td>
</tr>
<tr>
<td>Al-SBA-15</td>
<td>10</td>
<td>11.38</td>
</tr>
<tr>
<td>MZ-15</td>
<td>40</td>
<td>47.02</td>
</tr>
<tr>
<td>MZ-16</td>
<td>20</td>
<td>20.85</td>
</tr>
</tbody>
</table>

7.1.2 Nitrogen Adsorption-Desorption

Table 7.2 shows the various structural properties of the catalysts obtained from N\textsubscript{2} adsorption-desorption analysis. It is observed that among the aluminum-modified SBA catalysts, the highest surface area and the pore volume are obtained with Al-SBA-16(10)3 catalyst that was prepared using lower pH value of 3. The increased value of the pore volume was expected due to aluminum extraction described above. The composite zeolite nanoseed catalyst, MZ-16, having the mesoporous portion of SBA-16 is offering the highest surface area, pore volume, and pore size.
### Table 7.2 Structural properties of the Al-modified mesoporous catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(S_g) (\text{m}^2/\text{g})</th>
<th>(S_{\text{mi}}) (\text{m}^2/\text{g})</th>
<th>(\text{BJH } S_g) (\text{m}^2/\text{g})</th>
<th>(v_{\text{mp}}) (\text{cm}^3/\text{g})</th>
<th>(\text{BJH } v_p) (\text{cm}^3/\text{g})</th>
<th>(d_p) (\text{nm})</th>
<th>(\text{BJH } d_p) (\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-SBA-16(10)</td>
<td>220.98</td>
<td>5.81</td>
<td>219.5</td>
<td>0.0030</td>
<td>0.4866</td>
<td>9.389</td>
<td>8.868</td>
</tr>
<tr>
<td>Al-SBA-16(20)</td>
<td>110.01</td>
<td>5.65</td>
<td>101.5</td>
<td>0.0033</td>
<td>0.3426</td>
<td>13.17</td>
<td>13.51</td>
</tr>
<tr>
<td>Al-SBA-16(40)</td>
<td>488.30</td>
<td>–</td>
<td>252.0</td>
<td>–</td>
<td>0.3077</td>
<td>4.96</td>
<td></td>
</tr>
<tr>
<td>Al-SBA-16(10),3</td>
<td>585.32</td>
<td>89.73</td>
<td>368.3</td>
<td>0.0384</td>
<td>0.9469</td>
<td>7.51</td>
<td>10.28</td>
</tr>
<tr>
<td>Al-SBA-15</td>
<td>249.90</td>
<td>–</td>
<td>85.72</td>
<td>–</td>
<td>0.088</td>
<td>–</td>
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</tr>
<tr>
<td>MZ-15</td>
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<td>–</td>
<td>36.31</td>
<td>–</td>
<td>0.037</td>
<td>–</td>
<td>3.98</td>
</tr>
<tr>
<td>MZ-16</td>
<td>1014.0</td>
<td>17.6</td>
<td>1081.3</td>
<td>–</td>
<td>4.09</td>
<td>5.91</td>
<td>15.13</td>
</tr>
<tr>
<td>MZ-41</td>
<td>239.50</td>
<td>17.6</td>
<td>205.9</td>
<td>0.0058</td>
<td>0.6350</td>
<td>11.32</td>
<td>12.33</td>
</tr>
</tbody>
</table>

\(S_g\) is surface area by using BET method, \(S_{\text{mi}}\) is micropore area obtained by t-plot, \(\text{BJH } S_g\) is BJH adsorption cumulative surface area of the pore between 17Å and 3000Å width, \(v_{\text{mp}}\) is micropore volume obtained by t-plot, \(\text{BJH } v_p\) is BJH adsorption cumulative volume of the pore between 17Å and 3000Å width, \(d_p\) is adsorption average pore diameter \((4V/A)\) by BET, and \(\text{BJH } d_p\) is BJH adsorption average pore diameter \((4V/A)\).

Fig. 7.2 shows the \(\text{N}_2\) adsorption-desorption isotherms of the catalysts. Where the data are available a curve upgradation is observed for the catalysts at \(P/P_0<0.1\). This indicates type I isotherm in the low pressure range and suggests the nitrogen filling in the micropores of the catalysts [4, 6]. In the medium pressure range, a linear increase in the adsorbed amount with an increase in relative pressure shows the monolayer adsorption of \(\text{N}_2\) on the pore walls of the catalysts [4]. A steep increase in the adsorbed value, generally in the range of \(P/P_0\) equal to 0.60–0.90 shows the filling of the mesopores by nitrogen [4]. This attributes to the multilayer adsorption of \(\text{N}_2\) in the mesopores of these catalysts [4, 5]. The sharpness of the curve in this region as best seen with Al-SBA-16(10)\,3 is an indication of the uniformity of the pore size distribution [4, 6]. In the regions of higher pressure, the curves are ascribed to type IV isotherms with \(H_2\) hysteresis of the IUPAC classification. It is clearly seen that change in the \(\text{Si}/\text{Al}\) ratio and \(pH\) value of the gel has changed the structural nature of the catalysts. Nitrogen adsorption-desorption isotherms have confirmed the presence of mesopores of the catalysts along with some micropore regions.

### 7.1.3 Small Angle and Wide Angle XRD Analyses

Small angle X-ray diffraction patterns were taken in the range of 0.5–4°. Fig. 7.3 displays the small angle XRD of all the eight calcined catalysts. For Al-SBA-15 and MZ-15 there are three peaks in 20 range of 0.5–2° though the latter two peaks are very small and not noticeable in the figure. The three peaks are attributed to (100), (110), and (200) diffraction peaks, respectively, representing typical diffraction pattern of Al-SBA-15 type material [3, 7, 8].
Fig. 7.2 N$_2$ adsorption-desorption isotherms of the Al-modified mesoporous catalysts.
The small angle XRD patterns of Al-SBA-16(10) and MZ-16 show peaks at $2\theta < 1^\circ$ that reflect Im3m cubic structure [10, 11]. However, the other few related peaks are not clearly detected as observed by the other researchers [12, 13]. It might be resulted due to the insertion of aluminum into the mesostructures that resulted in the formation of a material with lower order [12]. Low angle XRD pattern of Al-SBA-16(40) shows a sharp peak at 0.89 corresponds to (110) reflection representing Im3m cubic structure [13]. Two weak peaks are
present at 1.37 (200) and 1.81 (211). Many small peaks have shown their existence at 2θ > 2. For Al-SBA-16(20) a peak is observed at 0.88 corresponds to (110) reflection. Small peaks are observed at 1.58 and 1.86 correspond to reflections at (200) and (211). X-ray diffraction pattern of Al-SBA-16(10)3 reflects a characteristic peak at 2θ = 1.15 that shows (110) reflection. Weak (200) and (211) reflections are present that may be attributed to the presence of low order structure resulted due to higher aluminum concentration [12]. For MZ-41 many small peaks are overlapped at 2θ = 2 that reflects the presence of mesoporous MCM-41 structure, however, (110) and (200) reflections are weak or absent that depict low order mesoporous structure also due to the presence of higher aluminum content. Among all the catalysts Al-SBA-16(40) with the lowest aluminum concentration has found to have highly ordered structure.

Fig. 7.4 shows the wide angle XRD patterns for all the eight catalysts in the range of 6–70°. For each catalyst, a broad hump at 2θ-value of about 23° is observed. It is a characteristic peak attributed to the presence of amorphous silica material in the catalysts. Among all these catalysts MZ-41 has been found to contain the increased crystalline phase.

![Wide angle XRD patterns of the Al-modified mesoporous catalysts](image)

Fig. 7.4 Wide angle XRD patterns of the Al-modified mesoporous catalysts: (a) Al-SBA-16(10), (b) Al-SBA-16(20), (c) Al-SBA-16(40), (d) Al-SBA-16(10)3, (e) Al-SBA-15, (f) MZ-16, (g) MZ-15, and (h) MZ-41.

### 7.1.4 FTIR Spectroscopy

Fig. 7.5 shows the simple FTIR spectra of Al-SBA-16(10), Al-SBA-16(40), Al-SBA-16(10)3, Al-SBA-15, MZ-15, and MZ-16. FTIR spectra of all the catalysts show a broad peak centered at 3425 cm⁻¹ which corresponds to the adsorbed water molecules and also due to the stretching vibration of the terminal Si–OH group [14]. Characteristic peaks observed at 1625 cm⁻¹, 1089 cm⁻¹, 804 cm⁻¹, and 454 cm⁻¹ are attributed to the flexural vibration of –OH...
group [14], absorption band of Si‒OH vibration [15], T‒O (where, T = Si or Al) symmetric stretching mode [8], and bending mode of tetrahedral Si‒O, respectively [14].

![FTIR Spectra](image)

**Fig. 7.5** FTIR spectra of the Al-modified mesoporous catalysts: a) Al-SBA-16(10), b) Al-SBA-16(40), c) Al-SBA-16(10)3, d) Al-SBA-15, e) MZ-15, and f) MZ-16.

Pyridine-adsorption FTIR spectra of the catalysts are shown in **Fig. 7.6.** All the catalysts show a characteristic peak around 1623 cm$^{-1}$ associated to the presence of strong Lewis bond [16]. This band is prominent in the case of Al-SBA-16(10), Al-SBA-16(10)3, Al-SBA-15, and MZ-15 but shown as small shoulders for the other two catalysts. A small peak is present at 1545 cm$^{-1}$ in Al-SBA-16(10), Al-SBA-16(10)3, and Al-SBA-15 assigned to the presence of pyridinium ion ring vibration bond of pyridine at Brønsted sites [16]. Also, a small peak is observed at 1495 cm$^{-1}$ associated to Lewis+Brønsted sites [17] for Al-SBA-16(10), Al-SBA-15, MZ-15, and Al-SBA-16(10)3. The same association is observed at 1480 cm$^{-1}$ for Al-SBA-16(40) and MZ-16. The latter two catalysts also show a small peak, a characteristic peak, at 1595 cm$^{-1}$ attributed to the presence of hydrogen bonded pyridine [16]. All the catalysts have predominantly strong acid sites.
Fig. 7.6 FTIR spectra of pyridine adsorbed Al-modified mesoporous catalysts: a) Al-SBA-15, b) Al-SBA-16(10), c) MZ-15, d) MZ-16, e) Al-SBA-16(40), and f) Al-SBA-16(10)3.

7.1.5 TEM Analysis
The TEM images of the catalysts are shown in Fig. 7.7. The images of Al-SBA-15, Fig. 7.7 (a and b) clearly show the ordered hexagonal arrays of mesopores with large uniform pores that are the characteristic features of Al-SBA-15 [3, 7, 8]. Hexagonal mesostructures are also evident in the TEM micrographs of MZ-15 composite catalysts, Fig. 7.7 (c and d). In this catalyst there are present well-connected nanocrystals of ZSM-5 along with the mesoporous framework. The micrographs of Al-SBA-16(10), Fig. 7.7 (e and f) show regular cubic pore structures [19], whereas the morphology of MZ-16 composite, Fig. 7.7 (g and h) displays regular mesostructures interlocked with small nanocrystals.
Fig. 7.7 TEM images of the Al-modified mesoporous catalysts: a and b) Al-SBA-15, c and d) MZ-15, e and f) Al-SBA-16(10), and g and h) MZ-16.
7.2 Hydrocracking Performance of the Catalysts

Fig. 7.8 and 7.9 show the results of the hydrocracking experiments over the Al-modified catalysts. Fig. 7.8 shows the results of the experiments for 60 min residence time and over most of the Al-modified mesoporous catalysts for three reaction temperatures (375°C, 400°C, and 425°C). Fig. 7.9, on the other hand, shows the results for 50 min residence time and over Al-SBA-15(20) and MZ-41 for only 400°C temperature. It is observed that at low reaction temperatures of 375°C and 400°C generally the performance of all the catalysts towards conversion is better than the thermal run.
Fig. 7.8 Results of the hydrocracking of model plastic mixture over Al-modified mesoporous catalysts. 650 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
At 375°C, Al-SBA-15 gives the highest conversion as well as the liquid yield with least yield of the gaseous product compared to the other catalysts and the thermal run. On the other hand at 400°C the catalytic reactions are mostly favored over Al-SBA-16(10)3 in terms of conversion. However, in terms of liquid yield MZ-16 is found to be the most efficient catalyst. It is observed that the zeolite nanoseeds introduction into the mesostructures results in increased activity and selectivity [20] of the composite MZ-16 as compared to its mesoporous Al-SBA-16(10) at the temperature of 400°C. At lower temperature of 375°C, Al-SBA-15 and its composite catalyst MZ-15 delivered increased conversion and liquid yield. On the other hand, at the reaction temperature of 400°C, the better results are obtained over Al-SBA-16(10)3 and the composite catalyst MZ-16. MZ-16 performing better than Al-SBA-16(10) suggests the introduction of nanoseeds has produced better activity and desired selectivity characteristics in the SBA-16 structure. The opposite is true for MZ-15. At the two lower temperatures (375°C and 400°C), comparing Al-SBA-16(10) and Al-SBA-16(10)3 with same Si/Al ratio, the latter synthesized with lower pH value has given higher conversion and higher liquid yield.

When the reaction temperature of 425°C is studied, the thermal run is found to be the most active and produces high yield of oil. This might occur due to the increased formation of coke over an active catalyst especially with large pores and at relatively high temperature of 425°C. As the conversion is based on THF insoluble solid residue that includes coke, the apparent conversion may decrease with an increase in temperature. It is observed that the
effect of the presence and type of catalyst generally decreased with an increase in temperature.

The FTIR spectra for the liquid samples are shown in Fig. 7.10. All the liquid samples show a choppy peak at 2900 cm\(^{-1}\) assigned to the presence of alkanes in these samples. The quantity of alkanes is the highest in the case of MZ-15. However, Al-SBA-16 and Al-SBA-15 both have produced lesser quantity of alkanes as compared to the other two catalysts. MZ-15 shows a peak at 2200 cm\(^{-1}\) assigned to bond stretching of C=H bond. Weak sharp peak observed at 1600 cm\(^{-1}\) assigned to the presence of C=C bond stretching is also observed in each case. However, the unsaturated components are observed to be the highest in the case of MZ-15 and the least in the case of Al-SBA-15. Al-SBA-15 therefore has shown the increased hydrogenation ability. There is a characteristic sharp peak observed between 1600–1450 cm\(^{-1}\) in all the catalysts which corresponds to the presence of aromatic double bond stretch. The amount of aromatic components is the highest with MZ-15 (the composite catalyst), however, its corresponding mesoporous form (Al-SBA-15) has shown to produce the least amount of aromatic components. Al-SBA-15 has therefore shown the highest saturation with least double bond in its liquid products.

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**Fig. 7.10 FTIR spectra of the n-heptane soluble liquids obtained by the hydrocracking of model plastic mixture over Al-modified mesoporous catalysts. 650 ml autoclave, 60 min residence time, 20 bar initial cold hydrogen pressure, 400°C of reaction temperature, and 20:1 feed to catalyst ratio (by weight).**
7.3 Summary

Eight Al-modified mesoporous catalysts are characterized and their hydrocracking performance is tested for a model plastic mixture. The Al-modification is carried out by Al insertion into the mesoporous structure of SBA-15 and SBA-16 and by making composites of zeolite nanoseeds with mesoporous SBA-15, SBA-16, and MCM-41. The characterization results showed that an increase in the Si/Al ratio leads towards more spherical nature of the particles in the formation of Al-SBA-16. Al-SBA-16(40) with the lowest aluminum presence and Al-SBA-15 have shown higher ordered structure. It is observed that the Si/Al ratio of the synthesized catalysts with gel pH of 7 is closer to the Si/Al ratio of the gel. However, the catalyst for which the pH of the gel was maintained at 3 instead of 7, the Si/Al ratio in the catalyst is found much higher due to aluminum leaching in the acidic medium. No sharp peaks are observed in the wide angle XRD analysis thus showing amorphous nature of the catalysts.

For the hydrocracking reactions, it is found that at lower temperature of 375°C, Al-SBA-15 and its composite catalyst MZ-15 has shown increased conversion and liquid yield whereas at the reaction temperature of 400°C, the better performance is exhibited by Al-SBA-16(10)3 and the composite catalyst MZ-16. MZ-16 has performed better than Al-SBA-16(10) showing the introduction of nanoseeds has induced better activity and desired selectivity in SBA-16 structure. The opposite can be said for the MZ-15. At the two lower temperatures (375°C and 400°C), comparing Al-SBA-16(10) and Al-SBA-16(10)3 with same Si/Al ratio, the latter prepared with lower pH value has shown higher activity and higher liquid yield. It is observed that the effect of the presence and type of catalyst is less important at the elevated temperature of 425°C.

References


Chapter 8

Hydrocracking Performance of the Five Best Catalysts with and without Metal Impregnation

In this chapter, five best performing catalysts along with HZSM-5 (CBV2314) for comparison are further tested against actual waste plastic mixture and virgin HDPE. The stability of these catalysts is also evaluated by reusing the spent catalysts for hydrocracking of the model plastic mixture. Moreover, these five catalysts are impregnated with 0.5wt% Pt to increase the hydrogenation-dehydrogenation ability of the catalysts. These platinum impregnated catalysts are then tested at three reaction temperatures (325°C, 350°C, and 375°C) in a 500 ml autoclave reactor. The n-heptane soluble liquids produced in these experiments are analyzed by GC-FID and by FTIR analysis. The spent five best catalysts with and without Pt impregnation are also analyzed by TGA technique. Moreover, some combination of metals is also impregnated over ZC-FP catalyst to compare the effect of different impregnated metals on the hydrocracking of the model plastic mixture.

8.1 Selection of the Best Performing Catalysts

Fig. 8.1 and Fig. 8.2 show the results of hydrocracking of model plastic mixture over the catalysts employed in the previous chapters. Based on the conversion (activity of a catalyst required to convert the plastic material) and yield of the useful liquid products (selectivity of a catalyst towards liquid yield with increased gasoline content), five best catalysts are selected for additional study. Fig. 8.1 and 8.2 show some close rivals especially at increased temperature of 400°C. However, overall, considering all the results, ZC-F, ZC-FP, ZC-P, BC27, and BC48 catalysts were selected as the best performing catalysts. HZSM-5 has also performed well with respect to activity but it has produced undesirable gas yields. HZSM-5 was therefore not selected among the best performing catalysts. However, it was also applied in some additional experiments for comparison and to observe its hydrocracking performance for HDPE and actual waste plastic mixture.

8.2 Hydrocracking Reactions over Five Best Catalysts without Metal Impregnation

8.2.1 Hydrocracking Reactions with HDPE

HDPE is selected as feed for further testing of the catalysts as it is the most difficult plastic to be cracked among the plastics present in the municipal waste.
Fig. 8.1 Summary of the results of hydrocracking reactions of model plastic mixture over various catalysts presented in the previous chapters. 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).

Fig. 8.2 Summary of the results of GC analysis of the n-heptane soluble liquids obtained by the hydrocracking reactions of model plastic mixture over various catalysts presented in the previous chapters. 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
Hydrocracking reactions of HDPE are performed at 400°C of reaction temperature, 60 min of reaction time, and 20 bar of initial cold hydrogen pressure. Fig. 8.3 shows the conversion and selectivity of the products obtained in hydrocracking of HDPE. For comparison the figure also shows the results with model plastic mixture (from previous chapters). For the HDPE hydrocracking, it is observed that nearly similar conversion of about 100% is obtained for each of the catalysts. The highest oil and liquid yields of 58.81wt% and the lowest gas yield of 33.16% are produced by BC27 catalyst. On the contrary, among the best performing catalysts, the lowest oil and liquid yields and the highest gas yield are produced over ZC-P catalyst. The amount of liquid product is decreased whereas the gas yield is increased in the order of BC27, BC48, ZC-F, ZCF-P, and ZC-P.

Fig. 8.3 Results of the hydrocracking reactions over selected catalysts with: A) HDPE and B) model plastic mixture. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, 400°C reaction temperature, and 20:1 feed to catalyst ratio (by weight).
It is found that for all the catalysts the hydrocracking reactions using HDPE (Fig. 8.3A) as the feed display nearly the same conversion, lower amount of liquid yield, and significantly higher gas yield compared to their corresponding reactions with model plastic mixture (Fig. 8.3B) under the same reaction conditions. This is reasonable and can be explained on the basis that the model mixture contains significant amounts of PS, PP, and LDPE which are expected to yield higher liquid products. Moreover, the interaction among the various plastics can result in the formation of higher liquid content found with the hydrocracking of model plastic mixture. Among the reactions using model plastic mixture, the highest liquid yield is produced by BC27 narrowly followed by BC48. Similar trend is observed with HDPE as BC27 produced the highest liquid followed by BC48 catalyst. Zeolite HZSM-5 catalyst and its composites (ZC-F, ZC-FC, and ZC-P) have shown to produce increased gas yield than that of zeolite beta composite catalysts (BC27 and BC48). This may be attributed to the smaller micropores present in HZSM-5 catalyst that are selective towards the smaller gaseous components.

Gas chromatography analysis of the n-heptane soluble portion, oil, obtained with HDPE is shown in Fig. 8.4. It is observed that the product obtained over all the catalysts is majorly selective towards gasoline. The ZC-P catalyst produced the highest gasoline fraction of 83.99%, followed by HZSM-5, ZC-FP, and BC-27. When compared to the gasoline yield for model plastic mixture under the same reaction conditions (Fig. 8.4B), it is found that the gasoline component for model plastic mixture and HDPE is nearly the same over HZSM-5, and ZC-FP. However, ZC-P produced greater amount of gasoline with HDPE whereas BC27 yielded increased amount of gasoline with model plastic mixture. For BC27, the amount of gasoline obtained with HDPE is reduced to 57.78% in comparison to 70.53% with model plastic mixture. However, for BC27 higher yields of light diesel and heavy diesel are obtained with HDPE.

8.2.2 Hydrocracking Reactions with Actual Waste Plastic

Fig. 8.5 shows the results of hydrocracking reactions with actual waste plastic mixture over different catalysts at 400°C of reaction temperature, 60 min of residence time, and initial cold hydrogen pressure of 60 min. It is shown that the maximum conversion of waste plastic mixture is obtained with HZSM-5 comparable to the conversions obtained over ZC-F, ZC-FP, and ZC-P. BC27 and BC48 have shown relatively reduced conversions. The highest gas yield with least amount of liquid product is obtained with HZSM-5. The highest liquid yield of 70.25wt% is produced by BC27 though comparable liquid yields are obtained over ZC-F,
ZC-FP, and BC-48. The liquid product is decreased in the order of BC27>BC48>ZC-FP>ZC-F>HZSM-5. BC27 also produced the lowest gas yield and therefore the highest ratio of liquid to gas yields. Among the HZSM-5 composite catalysts ZC-FP and ZC-F performed comparably with respect to both gas and liquid yields.

Fig. 8.4 Results of GC analysis of the n-heptane soluble liquids obtained by the hydrocracking reactions over selected catalysts with: (A) HDPE and (B) Model plastic mixture. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, 400°C reaction temperature, and 20:1 feed to catalyst ratio (by weight).
Comparing the performance of the catalysts with model plastic mixture, it is found that all the catalysts showed slightly lower conversion but increased liquid or oil to gas yield ratio with actual waste plastic mixture, i.e., higher liquid yield and lower gas yield to that of the model plastic mixture under the same reaction conditions. This might be attributed to the presence of some impurities such as detrimental heteroatoms and trace metals in actual waste plastic mixture that interfered with the cracking reaction and engaged with the highly active sites that resulted in a decrease in the conversion, reduced gas product, and better liquid yield.

The gasoline and diesel selectivity obtained over waste plastic mixture is shown in Fig 8.6. These results reveal that the highest gasoline yield (72.39%) is obtained using HZSM-5. The gasoline component decreased in the order HZSM-5 > ZC-P > ZC-F > ZC-FP > BC27 > BC48. The HZSM-5 catalyst and its composite catalysts are found highly selective towards gasoline fraction than that of zeolite beta composites (BC27 and BC48). Although, BC27 produced the highest liquid yield with actual waste plastic mixture, however, the gasoline fraction of its oil was significantly lower to that of ZC-FP, which produced higher liquid yield among the the HZSM-5 composite catalysts. When compared to model plastic mixture, Fig. 8.4B, it is found that all the catalysts produced lower gasoline over actual waste plastic mixture than by the corresponding reaction over model plastic mixture. This further strengthens the idea that the interference of impurities present in actual waste plastic resulted in inhibiting the effect of highly active sites of the catalysts during hydrocracking reactions with actual waste plastic mixture.
Fig. 8.6 Results of GC analysis of the n-heptane soluble liquids obtained by the hydrocracking reactions with actual waste plastic over selected catalysts. 500 ml autoclave reactor, 20 bar initial hydrogen pressure, 60 min residence time, 400°C reaction temperature, and 20:1 feed to catalyst ratio (by weight).

8.2.3 Stability Study of the Catalysts with and without Calcining the Catalysts

8.2.3.1 Hydrocracking Reactions with Dried Spent Catalysts

The stability of the catalysts was analyzed by reusing HZSM-5 and the five best performing catalysts for the hydrocracking reactions with model plastic mixture. The spent catalyst was obtained from an earlier hydrocracking experiment with model plastic mixture using 500 ml autoclave, 60 min of residence time, 400°C of reaction temperature, and 20 bar of initial cold hydrogen pressure. The spent catalyst was dried in an oven for 30 min at 120°C. The dried spent catalyst was mixed with the fresh catalyst in 1:1 ratio by weight in order to compensate the loss of the used catalyst and to maintain the same feed to catalyst ratio. The spent catalyst was then employed for the hydrocracking reaction with model plastic mixture under the same reaction conditions as discussed above. The results obtained are displayed in Fig. 8.7. It is observed that the hydrocracking experiments yielded nearly the same conversion for HZSM-5, ZC-P, ZC-FP, and ZC-F catalysts. However, BC27 and BC48 provided lower conversions in the stability test reaction as compared to their reactions over the fresh catalysts (Fig. 8.3B). The liquid yield of all the catalysts increased considerably with a significant decrease in the gas yield. In these reactions the highest liquid yield of 79.62% is produced by ZC-FP. The liquid yield is decreased in the order ZC-FP>ZC-P>ZC-F>HZSM-5>BC27>BC48. This corresponds to the reduction in the elevated cracking ability of the catalysts that may be caused by the coke deposition on the highly active sites of the catalysts by which the highly
active sites are rather masked. The overall cracking ability of the catalysts HZSM-5, ZC-P, and ZC-FP at this temperature is much less affected by the coke deposition than that of zeolite beta composite catalysts, BC27 and BC48, in which case the conversion of the plastic material is reduced considerably.

![Graph showing yield of gas, oil, liquid, and conversion for various catalysts](image)

**Fig. 8.7** Results of the hydrocracking reactions of model plastic mixture over spent catalysts. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 400°C reaction temperature, and 20:1 feed to catalyst ratio (by weight).

The gas chromatography analysis of n-heptane soluble liquids from the stability reactions is displayed in Fig. 8.8 below. When compared to the reactions over fresh catalysts (Fig 8.4B), it is found that the oil obtained over the spent catalysts contains considerably less quantity of the gasoline component. The spent catalysts are less selective towards gasoline than their corresponding fresh catalysts. The highest amount of gasoline is produced over HZSM-5 which is 64.16% and the gasoline yield is decreased in the order HZSM-5>ZC-F>ZC-P>BC27>BC48. BC27 and BC48 produced much lower gasoline and the highest quantity of heavy diesel where the used BC48 is more selective towards heavy diesel.
8.2.3.2 Hydrocracking Reactions with Calcined Spent Catalysts

The stability of the catalysts was further analyzed by reusing HZSM-5 and the five best performing catalysts for the hydrocracking reactions with model plastic mixture. This time the spent catalysts were calcined in air in order to remove carbonaceous deposits from the catalyst surface. Each of the calcined spent catalysts was mixed with equal amount by weight of the corresponding fresh catalyst and the experiments were performed under the same reaction conditions as discussed above. The results of hydrocracking reactions over the used and calcined catalysts are displayed in Fig. 8.9. It is observed that all the catalysts yielded nearly the same conversion of 100% as that of fresh catalyst in hydrocracking reaction using similar reaction conditions. The highest liquid yield is produced by BC27 which is 65.61%. The liquid yield is decreased in the order BC27>BC48>ZC-FP>ZC-F>ZC-P>HZSM-5. All the calcined spent catalysts produced higher gas yield and lower liquid yield in the same reaction with fresh catalysts as well as to that of the non-calcined spent catalysts. This may be assigned to the increase in active sites due to calcination that decomposes the coke deposited on the active sites of the catalysts. Also, some sintering of the particles may occur reducing the average pore size of the catalysts thereby generating increased amounts of gases with reduced quantities of liquids. It is, however, important to mention that the trends of the yields for the various catalysts are remained the same as that obtained with the fresh catalysts.
Fig. 8.9 Results of the hydrocracking reactions of model plastic mixture over calcined spent catalysts. 500ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, reaction temperature of 400°C, and 20:1 feed to catalyst ratio (by weight).

The gas chromatography analysis of the n-heptane soluble fraction obtained from the hydrocracking of model mixture using the calcined spent catalysts is shown in Fig. 8.10.

It is found that all the coked calcined catalysts have produced less gasoline to their corresponding fresh catalysts (Fig. 8.4B) and higher gasoline to that spent catalysts without calcination (Fig. 8.6). The coke removal due to calcination opened up the highly active sites.
of micropores to produce more gasoline fraction than that of the non-calcined spent catalysts. The highest gasoline fraction is produced over HZSM-5 equal to 66.61% followed by ZCF, ZC-FP, ZC-P, BC48, and BC27.

8.3 Hydrocracking Reactions over Five Best Catalysts with Metal Impregnation

8.3.1 Pt Metal Impregnated Catalysts

8.3.1.1 Characterization of the Pt Metal Impregnated Catalysts

The structural properties of Pt impregnated catalysts from nitrogen physisorption study are shown in Table 8.1. The highest surface area is found in PtBC27 followed by PtBC48. After the platinum impregnation the surface area of all the five catalysts is decreased. However, the decrease in surface area is more prominent in two composite catalysts of zeolite beta, i.e., PtBC27 and PtBC48. It is a considerable loss in surface area compared to the HZSM-5 composite catalysts, i.e., PtZC-F, PtZC-FP, and PtZC-P. Along with surface area, PtBC27 and PtBC48 both exhibit high BJH volume and between the two the highest BJH volume is present in PtBC48 indicating both these beta catalysts have the highest mesoporous content. PtZC-F, PtZC-FP, and PtZC-P exhibit higher micropore volume with smaller BJH volume. In these three catalysts, the micropore volume remains intact when compared with their corresponding catalysts without Pt impregnation. However, the BJH volume of these catalysts is greatly reduced. On the other hand, in PtBC27 and PtBC48, there is a great reduction of microporous volume after platinum impregnation. The reason for these observations corresponds to the effect of basic pH that was maintained during the platinum impregnation procedure. Mesoporous volume may be greatly reduced due to the basic pH of the impregnated solution. Recalcination of the catalysts when impregnated which may cause sintering and the presence of Pt crystallites within the micropores may contribute to the decrease in micropore volume of the catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_g$ (m$^2$/g)</th>
<th>$S_{mi}$ (m$^2$/g)</th>
<th>$BJH\ S_g$ (m$^2$/g)</th>
<th>$v_{mp}$ (cm$^3$/g)</th>
<th>$BJH\ v_p$ (cm$^3$/g)</th>
<th>$BJH\ d_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtZC-F</td>
<td>292.6</td>
<td>152.4</td>
<td>57.34</td>
<td>0.0711</td>
<td>0.0737</td>
<td>6.56</td>
</tr>
<tr>
<td>PtZC-FP</td>
<td>366.6</td>
<td>155.9</td>
<td>64.76</td>
<td>0.07482</td>
<td>0.0822</td>
<td>3.23</td>
</tr>
<tr>
<td>PtZC-P</td>
<td>366.9</td>
<td>208.4</td>
<td>66.51</td>
<td>0.0916</td>
<td>0.079</td>
<td>6.5</td>
</tr>
<tr>
<td>PtBC27</td>
<td>384.9</td>
<td>99.2</td>
<td>101.1</td>
<td>0.0131</td>
<td>0.1125</td>
<td>3.20</td>
</tr>
<tr>
<td>PtBC48</td>
<td>382.5</td>
<td>59.59</td>
<td>149.5</td>
<td>0.0231</td>
<td>0.1766</td>
<td>3.56</td>
</tr>
</tbody>
</table>

Wide angle X-ray diffraction patterns of the catalysts are displayed in Fig. 8.11. It is found that all the five catalysts show a crystalline structure suggesting that the crystalline structure
is retained after the impregnation with platinum metal. However, the crystallinity (intensity of diffraction) of these impregnated catalysts is decreased compared to crystallinity of their corresponding catalysts without impregnation. The decrease in the intensities of the peaks of impregnated catalysts indicates that the platinum metal is widely dispersed over whole surface of the catalysts. The presence of three new small peaks at 2θ of around 40, 67, and 82° show the presence of Pt crystallites on the surface of the catalysts. For BC27, the impregnated species are found to be amorphous or their crystal size is too small (less then 4 nm) to be detected by XRD analysis [1].

![Wide angle XRD patterns of the Pt impregnated catalysts](image)

Fig. 8.11 Wide angle XRD patterns of the Pt impregnated catalysts: a) PtZC-FP, b) PtZC-F, c) PtZC-P, d) PtBC48, and e) PtBC27.

The FTIR spectra of the five Pt impregnated catalysts is shown in Fig. 8.12. All the five platinum impregnated catalysts exhibit characteristic bands at 1063 cm⁻¹ and 437 cm⁻¹ that are assigned to T–O bond stretching vibration and bending vibration, respectively [2]. The band at 548 cm⁻¹ is significant in PtZC-FP and relatively weaker in the other catalysts shows the vibrational mode of typical zeolite structure with five or six membered ring T–O–T in zeolites [3]. It indicates that all the catalysts retain their zeolite structure where the zeolite framework is found to be more intact in PtZC-FP. The transmission band at 799 cm⁻¹ is attributed to T-O-T bond symmetric stretching [4].
8.3.1.2 Hydrocracking Reactions over Pt Impregnated Catalysts

The hydrocracking performance of the platinum impregnated catalysts for model plastic mixture is tested at three different temperatures as 325°C, 350°C, and 375°C and the results of the experimental findings are shown in Fig. 8.13. It is found that at the lowest temperature of 325°C, the highest conversion of 69.83% is produced by PtZC-FP while PtBC27 has the lowest conversion. The conversion is decreased in the order of PtZC-FP > PtZC-F > PtZC-P > PtBC48 > PtBC27. Although, PtBC27 and PtBC48 yielded the least conversion but they produced equivalent amount of liquid products (~22%) with extremely diminished amount of gaseous products. This shows their enhanced ability to convert model plastic mixture to liquid products. On the other hand, PtZC-FP, PtZC-F, and PtZC-P though showing increased conversion but they are more selective towards gas products.

At 350°C the maximum conversion of 88.90% is exhibited by PtZC-P which is followed by PtZC-F and PtZC-FP. Again, PtBC48 and PtBC27 showed the least conversion but increased selectivity towards liquids with decreased selectivity towards gaseous products. The highest liquid yield of 53.68% and the lowest gas yield of 13.75% are produced by PtBC27 that is followed by PtBC48. Moreover, PtZC-FP, PtZC-F, and PtZC-P were again able to have high conversions but at the cost of increased gas yields. This is especially true for PtZC-P which yielded the maximum gaseous products.
Fig. 8.13 Results of the hydrocracking of model plastic mixture over best performing catalysts with and without Pt impregnation. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
At 375°C, all the catalysts showed very high conversions. Apart from PtBC27 and PtBC48, all the other catalysts delivered 100% conversion. PtBC27 produced the highest liquid amount of 70.48wt% closely followed by PtBC48. PtBC48 yielded the least gaseous products. The catalysts PtHZSM-5, PtZC-F, PtZC-FP, and PtZC-P were highly selective towards gas yield and produced least quantity of liquid products.

At all temperatures it is observed that PtZC-P, PtZC-FP, and PtZC-P produced much higher gas yield as compared to PtBC27 and PtBC48. Structural properties of these catalysts in Table 8.1 show that PtZC-P, PtZC-FP, and PtZC-P have much less BJH volume as compared to PtBC27 and PtBC48. These catalysts have smaller mesoporous content and mostly comprised of micropores. Due to the presence of majority of the micropores in these catalysts they have produced increased gaseous products. On the other hand, PtBC27 and PtBC48 are highly selective towards liquid yield due to the presence of higher mesoporous content in them. This idea is further strengthened by the fact that PtHZSM-5, a microporous catalyst, produced the highest gas yield, much higher than any of its composite catalysts at 375°C reaction temperature.

Overall with increase in temperature, the conversion over each of the catalysts is increased. For PtZC-P, PtZC-FP, and PtZC-P catalysts the gas yield increases with increase in temperature whereas the liquid yield is only slightly varied. For PtBC27 and PtBC48, the liquid yield increased with an increase in temperature but the gas yield for the case of PtBC48 first increased and then virtually remained constant.
When compared to the catalysts without Pt impregnation it is observed that all the platinum impregnated catalysts showed higher conversion. Significantly increased selectivity towards gases and reduced selectivity of liquids are obtained over PtHZSM-5 and its platinum impregnated composites compared to their corresponding catalysts without Pt impregnation.

Gas chromatography analysis of n-heptane soluble liquids over platinum impregnated catalyst at three reaction temperatures is displayed in Fig. 8.14.

![Graphs showing GC analysis results](image)

Fig. 8.14 Results of GC analysis of n-heptane soluble liquids obtained by the hydrocracking of model plastic mixture over best performing catalysts with and without Pt impregnation. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).

Each catalyst shows adequate selectivity towards gasoline content. At 325°C and 350°C reaction temperatures, the highest gasoline fraction is produced by PtZC-P whereas at 375°C the highest gasoline fraction is obtained with PtBC27. PtZC-P catalyst exhibits the highest microporous volume than the other catalysts. These micropores facilitated the lower molecular weight molecules of gasoline to leave the active site which might be the cause for increased gasoline content at lower temperatures. It is observed that compared to the other Pt impregnated catalysts though PtBC27 and PtBC48 are found highly selective towards liquid yield but their selectivity towards gasoline is generally not better than the other catalysts.
Comparing the gasoline and diesel yields at 375°C between the catalysts with and without Pt impregnation (Fig. 8.14), it is observed that all the catalysts without Pt impregnation produced higher gasoline fraction compared to their corresponding platinum impregnated catalysts. Hydrogen in the presence of platinum metal may have quenched the free radicals formed by cracking that may have caused a decrease in the gasoline yield for the Pt impregnated catalysts.

The FTIR spectra of n-heptane soluble liquids obtained by hydrocracking of model plastic mixture at 375°C and over five best performing catalysts with and without Pt impregnation are shwon in Fig. 8.15. It is found that for all the catalysts there exists a choppy peak at 2900 cm\(^{-1}\). This corresponds to the presence of alkanes in the liquid samples. Among the catalysts without impregnation, Fig. 8.15A, the highest amounts of alkanes are observed with BC27. However, for platinum impregnated catalysts, Fig. 8.15B, the most alkanes are found with PtBC48. All the catalysts without impregnation show a small peak at 1600 cm\(^{-1}\) attributed to the presence of C=C bond stretching. The highest amount of unsaturated compounds is produced by BC27 and the lowest unsaturated compounds are produced by ZC-FP. Among the platinum impregnated catalysts, the highest unsaturated compounds exist in PtZC-P. All the other catalysts have negligible quantities of unsaturated compounds. The characteristic sharp peak between 1450 cm\(^{-1}\) and 1600 cm\(^{-1}\) in all the catalysts indicates the presence of aromatic double bond stretch. For the catalysts without impregnation, this peak is the highest with BC27 therefore showing the maximum aromatic content produced by BC27. However, this peak is relatively weak with ZC-FP and BC48. Among the platinum catalysts the highest aromatic content is present with PtBC48 and the least amount of aromatics is present with PtBC27.

When compared, it is observed that the oils obtained over platinum catalysts contain more alkanes and less unsaturated components than that of the oils from their corresponding catalysts with no Pt impregnation. Generally, all the catalysts after the platinum metal impregnation produced higher amounts of alkanes, less aromatic compounds, and negligible unsaturated compounds.
Activity and selectivity of PtBC27 is also evaluated by using it with actual waste plastic mixture and the results are compared to the performance of the catalyst with model plastic mixture under the same experimental conditions, Fig. 8.16. It is found that actual waste plastic mixture resulted relatively lower conversion, lower gas yield, and lower liquid yield compared to the model plastic mixture. The presence of heteroatoms and trace metals due to
stabilisers, colorant, etc., might have interfered with cracking reactions with actual waste plastic mixture that ultimately resulted in reduced conversion and reduced gas yield. As there is not significant reduction in conversion and liquid yield when PtBC27 is used with actual waste plastic mixture, it is recognized that PtBC27 could be an appropriate catalyst for the hydrocracking of waste plastics.

![Graph showing conversion and yield for model and actual waste plastic mixture](image)

Fig. 8.16 Results of the hydrocracking of model plastic mixture and actual waste plastic mixture over PtBC27. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, 375°C reaction temperature, and 20:1 feed to catalyst ratio (by weight).

The gas chromatography analysis of the oils obtained over model plastic mixture and actual waste plastic mixture using PtBC27 at initial hydrogen pressure of 20 bar, in 500ml autoclave reactor, with 60 min of residence time, and at reaction temperature of 375°C is displayed in Fig 8.17. It is observed that PtBC27 has produced high concentration of gasoline range components with both types of feedstocks. With actual waste plastic mixture it has given slightly decreased gasoline yield. 68.16% of gasoline is obtained with model plastic mixture compared to 65.76wt% with actual waste plastic mixture. These findings further suggest PtBC27 to be an appropriate catalyst for the hydrocracking of waste plastics.
8.3.2 Additional Metal Supported Catalysts

The catalytic performance of ZC-FP impregnated with different metals is evaluated by hydrocracking model plastic mixture at three reaction temperatures such as 325°C, 350°C, and 375°C, at initial cold hydrogen pressure of 20 bar, and 60 min residence time using 500 ml autoclave. The results of the hydrocracking experiments are shown in Fig. 8.18.

It is observed that at the lowest reaction temperature PtZC-FP has been found as the most active catalyst. The highest conversion and gas yield of 69.82% and 42.67%, respectively, are produced by PtZC-FP. The second most active catalyst is still a Pt containing catalyst, however, the inclusion of Pd with Pt has considerably improved the liquid selectivity with an added benefit of reduced gas selectivity. CoRuZC-FP catalyst is the least active catalyst whereas the performance of PdRuZC-FP catalyst and NiMoWZC-FP catalyst is virtually comparable. It is observed that compared to the reactions at lower temperatures, the gas selectivity increased more rapidly than the liquid selectivity at higher temperatures. This may be due to the addition of hydrogenation-dehydrogenation function which has increased the activity of the catalysts by increased dehydrogenation, at high temperature, of the initially formed fragments. It is important to note that dehydrogenation reaction rate increases with temperature and thereby generates more alkenes which are cracked at higher rates than their corresponding alkanes.
Fig. 8.18 Results of the hydrocracking reactions of model plastic mixture over various metal impregnated catalysts. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
At 350°C PdRuZC-FP catalyst has shown the highest activity though not much different than PtPdZC-FP catalyst. Both of these catalysts along with NiMoWZC-FP have delivered nearly the same liquid yields of about 32.0%. At the highest temperature of 375°C, it is observed that PtZC-FP shows 100% conversion closely followed by all the other catalysts. CoRuZC-FP catalyst has shown the highest selectivity towards liquid (43.13%) and also provided the least amount of gaseous products. NiMoWZC-FP catalyst has shown the least conversion, least liquid and oil selectivities, and very high gas yields. At this temperature, PtZC-FP, PdRuZC-FP, and NiMoWZC-FP catalysts are probably not the suitable catalysts for hydrocracking of plastics.

At all the temperatures the conversion and gas yield over each of the catalyst is considerably enhanced with increase in temperature. For PtZC-FP catalyst, the gas yield is always on the higher side and for CoRuZC-FP there is a substantial increase in liquid yield with increase in temperature. At 325°C PtPdZC-FP is found the most suitable catalyst whereas at the highest temperature CoRuZC-FP has shown the potential to be the most suitable catalyst for the hydrocracking reactions.

The GC analysis of the n-heptane soluble liquids obtained at 375°C is shown in Fig. 8.19. It is found that the highest gasoline selectivity is obtained by PtZC-FP. Although, CoRuZC-FP catalyst yielded the highest liquid amount at 375°C, but, the gasoline percentage in the liquid product is found less than that obtained with PdRuZC-FP and PtZC-FP catalysts.

![Fig. 8.19 Results of GC analysis of the n-heptane soluble liquids obtained by the hydrocracking of model plastic mixture over various metal impregnated catalysts. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, 375°C reaction temperature, and 20:1 feed to catalyst ratio (by weight).]
8.4 Thermogravimetric Analysis (TGA) of Spent Catalysts

The spent or used catalysts obtained in the hydrocracking of model plastic mixture at 375°C are examined by TGA. TGA is a temperature programmed technique in which weight loss of a material is studied by change in carefully controlled temperature. Fig. 8.20 shows the TGA results of the spent catalysts with and without Pt impregnation. For clarity of the findings, the TGA results are also summarized in Table 8.2 and Table 8.3.

![TGA results of spent catalysts](image)

Fig. 8.20 TGA results of the spent catalysts resulted from the hydrocracking of model plastic mixture conducted at 375°C reaction temperature, 500 ml autoclave reactor, 60 min of residence time, initial cold hydrogen pressure of 20 bar, and 20:1 feed to catalyst ratio (by weight): A) Without Pt impregnation, B) With Pt impregnation.
For each catalyst three clear thermal regions are observed. The weight change of the catalyst from 30–300°C corresponds to the desorption of the reactants/products, adsorbed in the pores of the catalysts [5]. The next most drastic weight loss centered at around 300°C to 450°C and another less significant weight lose from 450°C–600°C attributed to the decomposition of coke deposited on the catalyst pores. The coke decomposition at two temperature ranges indicates the presence of the two different types of coke deposited on the catalysts pores as soft coke and hard coke produced perhaps due to the deposition of paraffinic and aromatic coke deposition on the catalysts [6].

It is found that all the catalysts without impregnation produced significantly higher coke compared to their corresponding platinum impregnated catalysts. This indicates the higher hydrogenation ability of the platinum impregnated catalysts that inhibit the coke deposition by hydrogenating the unsaturated coke precursor species adsorbed on the surface of the catalysts.

Table 8.2 Weight loss of the catalysts without Pt impregnation in TGA experiments

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T&lt;300°C</th>
<th>300°C&lt;T&lt;450°C</th>
<th>T&gt;450°C</th>
<th>Total 30°C–600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZC-F</td>
<td>12</td>
<td>37.71</td>
<td>7.05</td>
<td>56.76</td>
</tr>
<tr>
<td>ZC-FP</td>
<td>9.59</td>
<td>62.15</td>
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<tr>
<td>ZC-P</td>
<td>3.53</td>
<td>31.65</td>
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</tr>
<tr>
<td>BC27</td>
<td>4.59</td>
<td>48.57</td>
<td>16.63</td>
<td>69.79</td>
</tr>
<tr>
<td>BC48</td>
<td>5.23</td>
<td>40.76</td>
<td>22.73</td>
<td>68.73</td>
</tr>
</tbody>
</table>

Table 8.3 Weight loss of the Pt impregnated catalysts in TGA experiments

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T&lt;300°C</th>
<th>300°C&lt;T&lt;450°C</th>
<th>T&gt;450°C</th>
<th>Total 30°C–600°C</th>
</tr>
</thead>
<tbody>
<tr>
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<td>36.73</td>
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<tr>
<td>PtZC-FP</td>
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</tr>
<tr>
<td>PtZC-P</td>
<td>10.29</td>
<td>14.24</td>
<td>2.06</td>
<td>26.59</td>
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<tr>
<td>PtBC27</td>
<td>16.15</td>
<td>23.46</td>
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<td>43.65</td>
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<tr>
<td>PtBC48</td>
<td>11.65</td>
<td>26.71</td>
<td>2.81</td>
<td>41.16</td>
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</tbody>
</table>

8.4 Summary

Out of all the catalysts used five catalysts are selected for further study on the basis of their activity and selectivity for liquid yield enriched with gasoline. With HDPE all the selected catalysts showed nearly the same conversion. The highest liquid yield is produced by BC27 (58.81%) catalyst but the gasoline content (57.78%) in the n-heptane soluble liquids obtained over BC27 is found much lower compared to the other catalysts. ZC-FP catalyst, however, produced considerably good liquid yield of 47.53% with much higher gasoline content of
77.67%. All the catalysts produced higher gas yield and lower liquid yield with HDPE in comparison to the identical reactions with model plastic mixture.

Hydrocracking reactions with actual waste plastic mixture showed lower conversion, higher liquid yield, and lower gas yield than their corresponding hydrocracking reactions with model plastic mixture. ZC-FP is found the best catalyst with 67.1% liquid yield and 67.15% of gasoline. ZC-FP has therefore potential to be used as a commercial catalyst for the hydrocracking of waste plastics.

With model plastic mixture, the FTIR results show that BC27 produced higher alkanes, unsaturated products, and aromatics whereas ZC-FP produced slightly lower amount of alkanes to that of BC27 with lower unsaturated and lower aromatic contents. The quality of ZC-FP is therefore better.

Catalyst stability data has revealed that HZSM-5 and its composite catalysts ZC-P, ZC-FP, ZC-F are highly promising catalysts to be reused. These catalysts are found highly active and produced same conversion when reused as either spent catalysts or calcined spent catalysts (the used catalysts are calcined before reusing). However, BC27 and BC48 showed considerably reduced conversion when reused without calcining. On the other hand all the six catalysts showed nearly the same conversion when their corresponding calcined spent catalysts are used in a similar reaction. The liquid yield of all the catalysts is generally higher when reused without calcining and in the experiments ZC-FP has found the best catalyst, showing possible feasibility for commercial purposes, with liquid yield of 79.62% containing gasoline of 50.93%. The calcined spent catalysts generally showed different results with increased gas production and reduced liquid production than that of their fresh catalysts. For these calcined spent catalysts, BC27 and BC48 produced higher liquid yields where BC27 is found the most promising catalyst with the lowest gas yield and the highest liquid yield of 65.61% containing gasoline of 56.51%.

All the catalysts showed a reduction in the surface area after platinum impregnation. It is observed that after platinum impregnation the catalysts showed higher conversion and produced higher gas yield than that of their corresponding catalysts without impregnation under the same conditions of reactions. However, the increase in gas yield is more drastic in the case of PtHZSM-5 and its composites catalysts (PtZC-F, PtZC-FP, PtZC-P), whereas for PtBC27 and PtBC48 there is a minor increase in gas yield with significant increase in the liquid yield. GC analysis shows that platinum impregnated catalysts produced lower gasoline with higher light diesel and heavy diesel components. Among the five platinum impregnated catalysts PtBC27 is found the most promising catalyst with the highest liquid yield at 350°C.
and 375°C and the least gas yield at all the reaction temperatures. GC analysis of oil obtained over this catalyst also shows the higher selectivity of this catalyst towards gasoline. Liquid FTIR of the oil shows that the quality of the oil is good over PtBC27 with lower aromatics and negligible unsaturated compounds than that of the other catalysts. PtBC27 was also tested with actual waste plastic mixture. With waste plastic mixture virtually similar performance was shown by the catalyst as that observed with model plastic mixture.

When compared it is observed that oils obtained over platinum catalysts produced more alkanes and negligible unsaturated components than that of the oils from their corresponding non-impregnated forms. All catalysts after platinum impregnation produced higher alkanes and less aromatic compounds and negligible unsaturated components. Within the platinum impregnated catalysts the highest alkanes are produced by PtBC48 with higher aromatic content as compared to the other catalysts. However, PtBC27 produced comparatively decreased amount of alkanes than that of PtBC48 but it yielded negligible unsaturated compounds and lower aromatics suggesting a better quality liquid product with PtBC27.

Impregnation of ZC-FP with different metals shows that at all the temperatures PtZC-FP produced the highest gas yield and CoRuZC-FP produced the lowest gas yield. The conversion over CoRuZC-FP catalyst is the lowest at 325°C and 350°C. However, at the highest temperature of 375°C, the conversion over CoRuZC-FP catalyst comes closer to the other catalysts with the highest liquid yield also. At 325°C and 350°C, the performance of PtPdZC-FP is extremely good in terms of conversion and liquid yield. However, at 375°C, the liquid yield of this catalyst is exceeded by CoRuZC-FP. GC analysis of oil at 375°C shows that the highest gasoline of 59.04% is produced over PtZC-FP. Although, CoRuZC-FP has shown to give the highest liquid yield at 375°C, however, the gasoline content of its oil is less than PdRuCZ-FP and PtZC-FP.

References


Chapter 9

Kinetics of the Hydrocracking Reaction of Model Plastic Mixture and Proposed Commercial Plant for the Hydrocracking of Waste Plastics

Kinetic modeling of the experimental data provides valuable information required for the design of a new commercial chemical reactor system. Once the intrinsic reaction kinetics are known any required type of the reactor may be designed. In this chapter, kinetic modeling for the hydrocracking reaction of the model plastic mixture over ZC-FP catalyst is carried out. Moreover, the concept of a commercial hydrocracking unit for waste plastics using a fluidized bed reactor is provided. The process flow diagram of the commercial hydrocracking unit is conceptualized.

9.1 Kinetics of the Hydrocracking Reaction of Model Plastic Mixture over ZC-FP Catalyst

9.1.1 Experimental Data

Experimental data over ZC-FP catalyst is obtained for various reaction temperatures, initial cold hydrogen pressures, feed to catalyst ratios (by weight), and residence times. The experimental data used in the kinetic modeling is shown in Table 9.1 and the representation of the data in graphical form to observe the effect of reaction operating conditions is shown in Appendix B.

Table 9.1 Experimental data for the kinetic modeling of hydrocracking of model plastic mixture over ZC-FP catalyst in 500 ml autoclave reactor

<table>
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<tr>
<th>Sr No</th>
<th>( t ) (day)</th>
<th>( W ) (kg)</th>
<th>( F ) (kg)</th>
<th>( T ) (K)</th>
<th>( pH2O ) (bar)</th>
<th>( Y_{gas} )</th>
<th>( Y_{oil} )</th>
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\[
\frac{dX}{dt} = k(X)^a \left( \frac{p_{\text{H}_2\text{O}}}{p^o} \right)^b \left( \frac{W}{F} \right)^c
\]  

(9.1)

Where, \(X\) is conversion of the plastic feed, wt\%; \(t\) is time of the reaction, s; \(k\) is rate constant \(s^{-1}\), \(p_{\text{H}_2\text{O}}\) is initial cold hydrogen pressure, bar; \(p^o\) is reference pressure taken as 1 bar; \(W\) is catalyst weight, kg; and \(F\) is plastic feed, kg; \(a, b,\) and \(c\) are regression parameters.

Integrating Eq. 9.1 between the limits at \(t = 0, X = 0\), and \(t = t, X = X\), it may be shown that

\[
X = \left[ \frac{kt}{a} \left( \frac{p_{\text{H}_2\text{O}}}{p^o} \right)^b \left( \frac{W}{F} \right)^c \right] \left( \frac{1}{1-a} \right) \quad \text{for } a \neq 1
\]  

(9.2)

\[
X = \exp \left[ \frac{kt}{a} \left( \frac{p_{\text{H}_2\text{O}}}{p^o} \right)^b \left( \frac{W}{F} \right)^c \right] \quad \text{for } a = 1
\]  

(9.3)

The temperature dependency is given by Arrhenius equation. In order to improve the numerical convergence the Arrhenius equation of the following form is used with Eq. 9.2 and Eq. 9.3.
\[ k = k_r \exp \left( B \left( 1 - \frac{T_r}{T} \right) \right) \] (9.4)

Where, \( k_r \) is rate constant at reference temperature, \( s^{-1} \); \( B \) is dimensionless activation energy (Eq. 9.5); \( T \) is reaction temperature, K; and \( T_r \) is reference temperature equal to 654.10 K, which is the average temperature of all the reaction temperatures used in the experimentation.

\[ B = \frac{E_a}{RT_r} \] (9.5)

Eq. 9.2 and Eq. 9.3 along with Eq. 9.4 are fitted against the experimental data to find out the regression parameters and the better kinetic model between Eq. 9.2 and Eq. 9.3. Activation energy is calculated using Eq. 9.5. SigmaPlot software is used for the regression of the data where SSE (the sum of squares of the errors) is used as the objective function to be minimized. \( R^2 \) and F-value of the models are also compared to find out the best-fit kinetic model. The following equations were used to calculate the statistical parameters.

\[ \text{SSE} = \sum_{i=1}^{i=N} (X_{\text{exp},i} - X_{\text{mod},i})^2 \] (9.6)

Where, \( X_{\text{exp},i} \) is observed or experimental value, \( X_{\text{mod},i} \) is calculated or model value, and \( N \) is total number of data points.

\[ F = \frac{\text{MSR}}{\text{MSE}} \] (9.7)

\[ \text{MSR} = \frac{\text{SSM} - \text{SSE}}{m - 1} \quad (m \text{ is number of parameters}) \] (9.8)

\[ \text{SSM} = \sum_{i=1}^{i=N} (X_{\text{exp},i} - \bar{X})^2 \] (9.9)

\[ \bar{X} = \frac{\sum_{i=1}^{i=N} X_{\text{exp},i}}{N} \] (9.10)

\[ \text{MSE} = \frac{\text{SSE}}{N - m} \] (9.11)
The results of the regression are shown in Table 9.2 and a parity chart is shown in Fig. 9.1. Clearly, model Eq. 9.2 is showing better fitting of the data. A relatively high value of $R^2$ of 0.866 suggests a good fit to the experimental data. The percentage error calculated by Eq. 9.13 is only $\pm 5.828\%$. The values of $a$, $b$, $c$, $E_a$, and $k_r$ are also given in Table 9.2. The apparent activation energy for the conversion of the model plastic mixture is obtained as 236.8 kJ/mol.

$$
R^2 = 1 - \frac{SSE}{SSM} \tag{9.12}
$$

Similar reasoning to that used in the development of Eq. 9.1 was also applied for modeling the experimental data of the yields of the products. The form of the equation used for kinetic modeling of the gas, oil, and liquid yields is shown below (Eq. 9.14):

$$
Y = \left[ k_t \left( \frac{P_{H_2O}}{p^c} \right)^b \left( \frac{W}{F} \right)^c (1-a) \right] \left( \frac{1}{1-a} \right) \quad \text{for } a \neq 1 \tag{9.14}
$$

The results of regression are shown in Table 9.2. The fits are generally good though slightly inferior to the fitting of the conversion data as suggested by somewhat lower values of $R^2$ and F-statistics. The percentage errors, calculated from Eq. 9.13, are 2.71\%, 6.74\%, and 5.91\%, respectively, for gas, oil, and liquid yields.
Table 9.2 Results of regression of the data obtained over ZC-FP catalyst

<table>
<thead>
<tr>
<th>Data fitting</th>
<th>Model equation</th>
<th>Statistical significance</th>
<th>Kinetic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>m  SSE  R²   F  %error</td>
<td>a  b  c  B  Eₐ (kJ/mol)  kᵢ (s⁻¹)</td>
</tr>
<tr>
<td>Conversion</td>
<td>[X = \left[ \frac{kt}{p^o} \right] \left[ \frac{P_{H₂O}}{p^o} \right]^b \left( \frac{W}{F} \right)^c (1-a) \left( \frac{1}{1-a} \right) ]</td>
<td>5  0.096  0.866  25.93  5.828  -5.7945  -0.1089  -0.5562  43.54  236.8  0.3815</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>a ≠ 1</td>
<td></td>
</tr>
<tr>
<td>Conversion</td>
<td>[X = \exp \left[ \frac{kt}{p^o} \right] \left[ \frac{P_{H₂O}}{p^o} \right]^b \left( \frac{W}{F} \right)^c ]</td>
<td>4  0.600  0.168  1.143  11.53</td>
<td>0.1260  -0.7115  -36.02  -195.9  -0.2263</td>
</tr>
<tr>
<td>Gas yield</td>
<td>[Y_{gas} = \left[ \frac{kt}{p^o} \right] \left[ \frac{P_{H₂O}}{p^o} \right]^b \left( \frac{W}{F} \right)^c (1-a) \left( \frac{1}{1-a} \right) ]</td>
<td>5  0.022  0.805  16.52  2.714  -3.7551  0.8838  0.5809  30.21  164.3  0.0111</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>a ≠ 1</td>
<td></td>
</tr>
<tr>
<td>Oil yield</td>
<td>[Y_{oil} = \left[ \frac{kt}{p^o} \right] \left[ \frac{P_{H₂O}}{p^o} \right]^b \left( \frac{W}{F} \right)^c (1-a) \left( \frac{1}{1-a} \right) ]</td>
<td>5  0.137  0.734  11.02  6.743  -4.7383  -0.7391  -0.2732  52.20  283.9  0.2227</td>
<td></td>
</tr>
<tr>
<td>Liquid yield</td>
<td>[Y_{liquid} = \left[ \frac{kt}{p^o} \right] \left[ \frac{P_{H₂O}}{p^o} \right]^b \left( \frac{W}{F} \right)^c (1-a) \left( \frac{1}{1-a} \right) ]</td>
<td>5  0.108  0.720  10.29  5.914  -6.2678  -0.9061  0.1899  53.42  290.5  0.1661</td>
<td></td>
</tr>
</tbody>
</table>
9.2 Proposed Commercial Plant for the Hydrocracking of Waste Plastics

Fig. 9.2 shows the process flow diagram for the proposed commercial plant for the hydrocracking of waste plastics. Waste plastic material after shredding, washing, and drying is transported to the hydrocracking reactor. The transportation of the waste plastics is caused by screw conveyors and the hydrocracking reactor is a fluidized bed reactor. A fluidized bed reactor can accept a solid feed and maintains uniform temperature throughout the reaction vessel. It is also easy to insert heating coils if increased temperature is required or the temperature drops due to the reaction. Hot nitrogen and hydrogen are fed from the bottom of the reactor to fluidize the catalyst particles and the plastic feed. Hydrogen is also used for the hydrocracking reaction of the plastics. A rapid increase in temperature of the plastic feed
Fig. 9.2 Proposed commercial process flow diagram for the hydrocracking of waste plastic.
quickly changes the solid plastic feed to the gaseous phase. The hot reaction products which are gases at the reaction temperature along with some fine catalyst particles leave at the top. It is important to mention here that the particle size of the catalysts in fluidized bed reactors is usually kept small for easy fluidization. The small particles also offer decreased diffusional resistances. At the downstream of the reactor, a cyclone separator is used to separate the catalyst particles and to send them back to the fluidized bed reactor. The reaction products leaving the cyclone separator are cooled to separate non-condensable gases from the rest of the product. The gas product leaving the cyclone is therefore cooled down by two process exchangers exchanging heat with the recycle gas which needs to be heated. The cooled product goes to a cooler which further decreases the temperature to an extent that a gas-liquid mixture is formed. The gas-liquid mixture is then sent to a high pressure flash drum and principally hydrogen gas is removed. The objective of high pressure flash unit is to save energy of compression for the recycle gas and to avoid the loss of heavier hydrocarbons along with the gas leaving the separator at the top. The liquid product from the separator goes to the low pressure flash separator. A let down valve is used to decrease the pressure of the liquid. In the low pressure separator, most of the gases are expected to leave at the top and the heavy liquid stream leaves at the bottom. The bottom product goes to a distillation column where the liquid is fractionated into the desired liquid fuels such as gasoline, light diesel, and heavy diesel. The non-distillable product is available at the bottom while the non-condensable gases are obtained from the top of the reflux drum or accumulator. The gases leaving the low pressure flash unit are mixed with the recycle stream, compressed to the desired pressure, and heated to enter the fluidized bed reactor. A purge stream is there to maintain the concentration of hydrocarbons in the reactor system.

9.3 Summary
Kinetic modeling is carried out for the experimental data obtained over ZC-FP catalyst. The experimental data of conversion and yields of gas, oil, and liquid is fitted by a simple power law model. The kinetic model is found suitable in representing the experimental data. In each case of conversion and yields of gas, oil, and liquid, less than 7% percentage error, calculated from Eq. 9.13, is obtained. The activation energy for the conversion of model plastic mixture to reaction products is found to be 236.8 kJ/mol.

A possible solution for a commercial unit of waste plastic hydrocracking is presented.
Chapter 10
Conclusions and Future Work

A number of conclusions can be drawn from this study. The specific conclusions are already described at the end of each chapter. However, some important conclusions can be reiterated in this chapter. After the conclusions section future recommendations are provided for the interested researcher in a follow up work.

10.1 Conclusions
For the USY composite catalysts, the conversion and liquid yield for all the composite catalysts are found better than commercial USY catalyst. It is observed that the TEOS/USY ratio and the type of the mesophase affect the structure as well as the hydrocracking performance of the composite catalysts. It is found that the crystallinity of the catalysts is decreased with an increase in TEOS/USY ratio. UC0.75 catalyst with the lowest TEOS/USY ratio is found the best catalyst at lower temperature of 375°C. Now as the temperature is increased UC1.2 has shown increase in the conversion and oil and liquid yields. UC1.2 is synthesized with the highest TEOS/USY ratio. Comparing UC1.2 and US1.2 having the same TEOS/USY ratio but different mesophase, UC1.2 has shown better performance. For the composite USY catalysts, at very high temperatures, the effect of the type of catalyst is not found important.

Among the ZSM-5 composite catalysts, ZC-P catalyst is formed with highly ordered structure whereas comparatively less ordered structure is observed in ZC-FP. During the synthesis the composite catalysts kept the microporous crystallinity of HZSM-5. In the hydrocracking testing of the catalysts, overall ZC-FP is found the best catalyst. Although, ZC-P is found more active at lower temperature of 350°C than ZC-FP but ZC-FP has delivered greater liquid yield even its conversion is lower at that temperature. The n-heptane solubles show that both HZSM-5 and ZC-FP contain high content of gasoline fraction. However, HZSM-5 due to its microporous nature is found highly selective towards gaseous product.

The results of catalyst characterization with the composite catalysts of zeolite beta have shown that the crystalline structure of zeolite beta has been significantly destroyed by the desilication process. However, the composite catalysts without desilication treatment exhibit the crystalline structure of zeolite beta. The performance of these desilicated catalysts (BC11.1, BC5.7, and BC0.7) is found inferior to even zeolite beta and BA1 in terms of
conversion and liquid yield. Out of all the HZSM-5 based catalysts BC48 and BC27 found the most efficient catalysts with respect to conversion and liquid yield containing increased amount of gasoline.

The characterization results of Al-modified catalysts have revealed that an increase in the Si/Al ratio leads towards more spherical nature of the particles in the formation of Al-SBA-16. Al-SBA-16(40) with the lowest aluminum quantity and Al-SBA-15 have shown highly ordered structure. For the hydrocracking reactions, it is found that at lower temperature of 375°C, Al-SBA-15 and its composite catalyst MZ-15 has shown increased conversion and liquid yield whereas at the reaction temperature of 400°C, the better performance is exhibited by Al-SBA-16(10)3 and the composite catalyst MZ-16. At the two lower temperatures (375°C and 400°C), comparing Al-SBA-16(10) and Al-SBA-16(10)3 with same Si/Al ratio, the latter prepared with lower pH value has shown higher activity and higher liquid yield. It is observed that the effect of the presence and type of catalyst is less important at the elevated temperature of 425°C.

Out of all the catalysts mono-functional or catalytic supports discussed above, five catalysts, namely, ZC-F, ZC-FP, ZC-P, BC27, and BC48 are selected for further study on the basis of their better activity and selectivity of liquid yield enriched with gasoline. With HDPE all the selected catalysts showed nearly the same conversion. The highest liquid yield is produced by BC27 catalyst but the gasoline content in the n-heptane soluble liquids obtained over BC27 is found much lower compared to the other catalysts. ZC-FP catalyst, however, produced considerably good liquid yield with much higher gasoline content. All the catalysts produced higher gas yield and lower liquid yield with HDPE in comparison to the identical reactions with model plastic mixture. Hydrocracking reactions with actual waste plastic mixture showed lower conversion, higher liquid yield, and lower gas yield than their corresponding hydrocracking reactions with model plastic mixture. ZC-FP is found the best catalyst with higher amount of liquids and greater gasoline yield. ZC-FP has therefore potential to be used as a commercial catalyst for the hydrocracking of waste plastics. Compared to BC27, the quality of liquid yield is also found better with ZC-FP. The catalyst stability data has revealed that HZSM-5 and its composite catalysts ZC-P, ZC-FP, ZC-F are highly promising catalysts to be reused. However, BC27 and BC48 showed considerably reduced conversion when reused without calcining. The liquid yield of all the catalysts is generally higher when reused without calcining and in the experiments ZC-FP has found the best catalyst. The calcined spent catalysts generally showed different results with increased gas production and reduced liquid production than that of their fresh catalysts. For these
calcined spent catalysts, BC27 and BC48 produced higher liquid yields where BC27 is found the most promising catalyst with the lowest gas yield and the highest liquid yield.

All the catalysts have shown reduction in the surface area after platinum impregnation. It is observed that after platinum impregnation the catalysts showed higher conversion and produced higher gas yield than that of their corresponding catalysts without impregnation under the same conditions of reactions. However, the increase in gas yield is more drastic in the case of PtHZSM-5 and its composite catalysts (PtZC-F, PtZC-FP, PtZC-P) whereas for PtBC27 and PtBC48 there is a minor increase in gas yield with significant increase in the liquid yield. It is found that the platinum impregnated catalysts produced lower gasoline with higher light diesel and heavy diesel components. With actual waste plastic mixture PtBC27 has shown virtually similar performance that observed with model plastic mixture. When compared it is observed that oils obtained over platinum catalysts produced more alkanes and negligible unsaturated components than that of the oils from their corresponding non-impregnated forms. Within the platinum impregnated catalysts the highest alkanes are produced by PtBC48 with higher aromatic content as compared to the other catalysts. However, PtBC27 produced comparatively decreased amount of alkanes than that of PtBC48 but it yielded negligible unsaturated compounds and lower aromatics suggesting a better quality liquid product with PtBC27.

Impregnation of ZC-FP with different metals shows that at all the temperatures PtZC-FP has shown increased selectivity towards gaseous product. The conversion over CoRuZC-FP catalyst is the lowest at 325°C and 350°C, however, at the highest temperature of 375°C, the conversion over CoRuZC-FP catalyst reached closer to the other catalysts with the highest liquid yield also. At 325°C and 350°C, the performance of PtPdZC-FP is extremely good in terms of conversion and liquid yield whereas at 375°C, the liquid yield of this catalyst is exceeded by CoRuZC-FP. Although, CoRuZC-FP has provided the highest liquid yield at 375°C, however, the gasoline content of its oil is less than PdRuCZ-FP and PtZC-FP.

The experimental data of conversion and yields of gas, oil, and liquid taken over ZC-FP catalyst for model plastic mixture is fitted by a simple power law model. The kinetic model is found appropriate in representing the experimental data. The activation energy for the conversion of model plastic mixture to reaction products is found to be 236.8 kJ/mol.

A conceivable idea of a commercial unit for hydrocracking of waste plastics is presented.
8.2 Future Recommendations

In relation to the present work, below are some valuable future directions:

- The quantity of mesoporous template in the composite of ZSM-5 and beta could be increased in the future to study the effect of higher mesoporosity in composite catalysts on the catalyst performance.
- The ratio of P-123 and F-127 could be varied in ZC-FP, BC27 and BC48 to determine an optimum ratio, based on their activity and selectivity. In the current study a fixed ratio 1:1 (P-123:F-127) is used.
- Different molarities of NaOH solution could be used by future researchers for desilication treatment of ZSM-5 composite catalysts for obtaining an optimum molarity for the desilication.
- Reactions of the best supports could be performed at different reaction temperatures and different residence times to obtain the optimum reaction conditions with actual waste plastic mixture.
- BC27 could be impregnated with different weight percent of platinum and other metals to find the optimum weight ratio giving the best catalyst activity and selectivity.
- Catalysts stability study could be extended with and without regeneration with calcination.
- PtBC27 could further be studied at different temperatures and residence times with actual waste plastic mixture to evaluate the optimum reaction conditions with actual waste plastic sample.
- Stability experiments of PtBC27 could be performed on actual waste plastic.
- Work could be extended by using different commercial zeolites other than those used in this work.
- Municipal waste plastic sample from a waste management company could be taken as feed for actual representation of the process.
- Rather detailed kinetic study could be carried out to study the mechanism and to develop a more rigorous kinetic equation for better design of the commercial reactor system.
- The proposed process flow diagram for the hydrocracking of waste plastics could be simulated considering the kinetics of the reaction to workout the material and energy balances and the sizes of the equipments. A detailed parametric study can be carried
out to optimize the process conditions and to provide the design details of the process for the commercial facility.

- A pilot scale plant can be erected based on the simulation results and further experimentation at the pilot scale can be carried out.
### Appendix A

**Experimental Data of the Previous Researchers**

Table A-1 Experimental data of the previous researchers for the hydrocracking of plastic materials by the direct liquefaction method

<table>
<thead>
<tr>
<th>Plastic</th>
<th>$M$ (g/mol)</th>
<th>$T$ (°C)</th>
<th>$P_{H2,0}$ (MPa)</th>
<th>$t$ (min)</th>
<th>Catalyst</th>
<th>$F/C$ (wt/wt)</th>
<th>$X$ (wt%)</th>
<th>$Y_{gas}$ (wt%)</th>
<th>$Y_{liquid}$ (wt%)</th>
<th>$Y_{oil}$ (wt%)</th>
<th>Ref.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>125000</td>
<td>350</td>
<td>3.55</td>
<td>60</td>
<td>No catalyst</td>
<td>–</td>
<td>&lt;0.5s</td>
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<td>2.39i</td>
<td>2.1</td>
<td>0.90t</td>
<td>0.90h</td>
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</tr>
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<td>3.0i</td>
<td>2.1</td>
<td>0.90t</td>
<td>0.90h</td>
<td>[82]</td>
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<td>100n</td>
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<td>34.4cf</td>
<td>C1–C4</td>
<td>64.7cf</td>
<td>C5–C12</td>
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<td>60</td>
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*See Chapter 2

C = catalyst, F = feed, M = molecular weight, $p_{\text{H}_2}$ = H₂ pressure given initially at cold conditions, $t$ = reaction time, $T$ = temperature, $X$ = conversion, $Y$ = yield

Conversion: Converted plastic per 100% of plastic. Generally, the converted plastic includes gas and total liquid product.

Liquid: Total liquid including light and heavy liquid fractions, generally, that is soluble in THF.

Oil: A rather lighter fraction of the liquid such as that is soluble in n-pentane, n-hexane, etc.

ACB = activated carbon from biomass, ACC = activated carbon made from coal, ACW = activated carbon made from wood, $c$ = cyclohexane solubles, CA = citric acid, $ce$ = centrifuged, $cf$ = coke free basis, i.e., coke not included in the calculations, $d$ = dichloromethane solubles, $f$ = final hydrogen pressure, $gaso$ = gasoline range product, $h$ = n-hexane solubles, $hb$ = based on bp>360°C, $ht$ = n-heptane solubles, $i$ = initial hydrogen pressure (at reaction temperature), $la$ = lower alkanes, $lb$ = bp<360°C, n = based on residue not defined, $p$ = based on n-pentane solubles, $pi$ = n-pentane insoluble material, $s$ = based on solid residue, $t$ = based on THF solubles, $ti$ = based on THF insoluble material, $tm$ = based on THF+methanol insoluble residue (centrifuged), $un$ = unreacted plastics
Appendix B

Effect of Operating Variables on Hydrocracking of Model Plastic Mixture over ZC-FP Catalyst

B.1 Effect of Catalyst Amount

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Fig. B.1 Effect of the amount of ZC-FP catalyst in the hydrocracking of model plastic mixture for a fixed amount of 10 g plastic feed on the conversion and yields of the products. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 375°C reaction temperature.

B.2 Effect of Reaction Time

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</table>

Fig. B.2 Effect of residence time in the hydrocracking of model plastic mixture over ZC-FP catalyst on the conversion and yields of the products. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, and 20:1 feed to catalyst ratio (by weight).
Fig. B.2 Continued.
B.3 Effect of Hydrogen Pressure

Fig. B.3 Effect of initial cold hydrogen pressure in the hydrocracking of model plastic mixture over ZC-FP catalyst on the conversion and yields of the products. 500 ml autoclave reactor, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
B.4 Effect of Reaction Temperature

Fig. B.4 Effect of temperature in the hydrocracking of model plastic mixture over ZC-FP catalyst on the conversion and yields of the products. 500 ml autoclave reactor, 20 bar initial cold hydrogen pressure, 60 min residence time, and 20:1 feed to catalyst ratio (by weight).
Appendix C

Research Publications

Under Review


Published


Conference Proceedings