CHAPTER I

INTRODUCTION

1.1 Background

Plastic materials are presented in almost every field of daily life, and their consumption is predicted to show an annual growth rate of approximately 4% (from 25.9 million tones in 1996 to 36.9 million tones in 2006) [1]. In the UK, a total of approximately 4.7 million tones of plastic products are used in various economic sectors. Packaging represents the largest single sector of plastics use in the UK. The sector accounts for 35% of UK plastics consumption and plastic is the material of choice in nearly half of all packaged goods [2].
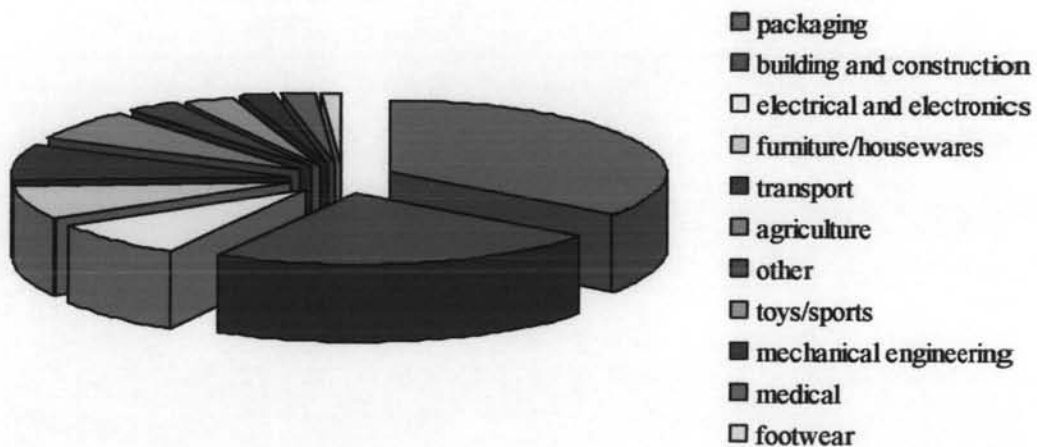

□ packaging
■ building and construction
□ electrical and electronics
□ furniture/housewares
■ transport
□ agriculture
■ other
□ toys/sports
■ mechanical engineering
■ medical
□ footwear

Figure 1.1 Plastic applications.

There are many types of plastic in common use. Plastic must be sorted by type for recycling since each type melts at a different temperature and has different properties. The plastics industry has developed an identification system (or identification codes) to label the different types of plastic. The identification system

divides plastic into seven distinct types and uses a number code generally found on the bottom of containers. The following table explains the seven code system.

Table 1.1   Types of plastic and their uses

Plastic Identity Code	Name of plastic	Description	Some uses for virgin plastic	Some uses for plastic made from recycled waste plastic
PETE 1	polyethylene terephthalate PET	Clear tough plastic, may be used as a fibre.	Soft drink and mineral water bottles, filling for sleeping bags and pillows, textile fibres.	Soft drink bottles, (multi-layer) detergent bottles, clear film for packaging, carpet fibres and fleecy jackets.
HDPE 2	high density polyethylene HDPE	Very common plastic, usually white or colored.	Crinkly shopping bags, freezer bags, milk and cream bottles, bottles for shampoo and cleaners, milk crates.	Compost bins, detergent bottles, crates, mobile rubbish bins, agricultural pipes, pallets, kerbside recycling boxes.
3 V	unplasticised polyvinyl chloride UPVC	Hard rigid plastic, may be clear.	Clear cordial and juice bottles, blister packs, plumbing pipes and fittings.	Detergent bottles, tiles, plumbing pipe fittings.
	plasticised polyvinyl chloride PPVC	Flexible, clear, elastic plastic.	Garden hose, shoe soles, blood bags and tubing.	Hose inner core, industrial flooring.
LDPE 4	low density polyethylene LDPE	Soft, flexible plastic.	Lids of ice cream containers, bin bags, rubbish bins, black plastic sheet.	Film for builders, industry, packaging and plant nurseries, bags.

Table 1.1   **Types of plastic and their uses**

♳ 5 PP	polypropylene PP	Hard, but flexible plastic - many uses.	Ice cream containers, potato crisp bags, drinking straws, hinged lunch boxes.	Compost bins, kerbside recycling boxes, wormeries.
♴ 6 PS	polystyrene PS expanded polystyrene EPS	Rigid, brittle plastic. May be clear, glassy. Foamed, lightweight, energy absorbing, thermal insulation.	Yogurt containers, plastic cutlery, imitation crystal "glassware". Hot drink cups, takeaway food containers, meat trays, packaging.	Clothes pegs, coat hangers, office accessories, spools, rulers, video/CD boxes.
♹ 7 OTHER	Includes all other plastics, including acrylic and nylon. These cannot be recycled.			

Plastic has benefited our society in a number of ways [3]. In fact, plastic has helped aeronautics technology take giant steps forward over the past 50 years. In addition, the building and construction, electronics, packaging, and transportation industries have all benefited greatly from plastic. The considerable growth in plastic use is due to the properties of plastics. These include:

- Lighter weight than steel and other materials that they replace, and lower vehicle weight significantly reduces fuel consumption.
- Extreme durability.
- Resistance to chemicals, water and impact.
- Good safety and hygiene properties for food packaging.
- Excellent thermal and electrical insulation properties.
- Relatively inexpensive to produce.
- Easily combined with other materials.

The consumption of plastic materials has been growing steadily. Plastic is a very useful commodity consumed in many aspects of human life in large volumes.

Nowadays, governments and environmental foundations have to take into consideration, more and more, the generation of large amounts of plastic waste as they cause serious pollution. Most plastic wastes are disposed of by landfill or incineration [4]. Plastic waste being more voluminous than the organic waste takes up a lot of landfill space that is becoming scarce and expensive. Incineration is not an acceptable solution to the problem, as toxic gases are produced and a solid waste problem becomes air pollution. The only sustainable solution is plastic recycling. Between various plastic recycling methods, thermal and/or catalytic degradation of plastic waste to fuel show the highest potential for a successful future commercial process, especially as plastic waste can be considered as a cheap source of raw materials in times of accelerated depletion of natural resources.

An alternative strategy is that of chemical recycling, which has attracted much interest recently with the aim of converting waste polymer wastes into basic petrochemicals to be used as feedstock or fuel for a variety of downstream processes. Two main chemical recycling routes are the thermal and catalytic cracking of plastic waste [5].

1. Thermal cracking involves the degradation of the polymeric materials by means of temperature when it is applied under inert atmosphere conditions [6]. In term of mechanism, it precedes a radical chain reaction pathway with hydrogen transfer steps. Normally, no rearrangement reactions occur, while branched products are only formed in secondary reactions as a result of the interaction two radicals. As a consequence, it produces a broad product range and required high operating temperature, typically more than 500°C and even up to 900°C.

2. Catalytic cracking involves several advantages over a purely thermal process. First, catalyst promotes the degradation reaction to occur at lower temperatures with lower energy consumptions. Second and most importantly, the shape selectivity allows the formation of narrower distribution of products, which may be directed towards light and aromatic hydrocarbons with higher market values. It provides to control the product distribution and reduce the reaction temperature.

Polyolefins belong to the most growing industrial polymers. In 2005, around 100 million tonnes of polyethylene and polypropylene were produced. For 2010, it is estimated that the production will reach 130 million tones [7]. Polyolefins, similar as

other plastics are produced from oil components, could be discussed as an intermediate use of crude oil as solid hydrocarbons. A high percentage of plastics end its lifetime as a part of the overall solid waste stream. The typical distribution of plastics in household waste is polyolefins 66.9%, polystyrene 13.3%, PVC 10.3%, PET 5.3%, and others 4.2%. Polyolefins as the main waste fraction consist of carbon and hydrogen only. This makes them extremely suitable for feedstock recycling with the production of valuable hydrocarbon products.

Polypropylene (PP) is one of the fastest growing polymers in the world. A recent market research report expects PP consumption to reach 51 million tones by the end of this decade (2010). Its position as the largest polyolefin will remain the top ranking polyolefin until 2010. The growth can be tied to the increasing applications in food packaging and auto component markets besides the existing wider application range. Injection moulding will continue to be the largest as well as the fastest growing end use segment with a compounded annual rate of 6.4%. Extrusion end-use industry represents the second largest application for PP. These two sectors will contribute to more than 90-95% of PP's processing sectors.

Asia Pacific region represents the largest market for PP with an estimated consumption of 16.8 million metric tons in 2007 and following by Europe and the United States. Collectively, the three regions are estimated to account for more than 75% of the global consumption of PP. Asia-Pacific region is also projected to be the fastest growing market with following by South America. China continues to be the most significant importer of polypropylene and drives the market for PP along with India.

The principal characteristics of polypropylene that have contributed to its rapid growth and acceptance are:

- Relatively high stiffness, low specific gravity (0.900-0.906 g/cc)
- High tensile strength (especially when oriented), good clarity, stress crack resistance, chemical resistance and relatively high heat deflection temperature.
- Mechanical strength properties, when filled or reinforced sufficient to compete with more costly engineering plastics in many applications.
- Good injection molding characteristics.
- Ability to be drawn and oriented, which is the basis for the production of polypropylene fibers and oriented film.

The researchers have contributed to the theory and practice of thermal degradation (with or without catalyst) of polymers. Mainly polyolefins, polyethylene (PE) and polypropylene (PP) and polystyrene (PS), are the target polymer, because their cracking results in products with favourable properties for further application [8]. According to results the products of polyethylene, polypropylene and even polystyrene cracking have the most favourable properties for further energetic applications. PE derived fuel has very high cetane and octane number, because it is rich in linear paraffins and olefins. Linear paraffin content in the gas oil fraction is advantageous, because this hydrocarbon structure has the highest cetane rate, but also has the lowest octane number in the naphtha fraction. However, PE-derived naphtha-like fraction has high octane number, which comes from the high content of olefins. The liquid products of PP cracking contain primarily olefins and isoparaffins that resemble the molecular skeleton of PP. Both hydrocarbon structures are advantageous for further utilization. Neat PS feedstocks will depolymerise in cracking processes to give predominately styrene monomer. Therefore, the fuel made from polystyrene feedstock will be high by aromatic character and have good energy content. The aromatic hydrocarbons have the highest octane number in the naphtha fraction [9].

An interesting alternative is based on the use of solid-acid catalysts to promote the catalytic degradation of plastic waste, thereby offering considerable advantages. It occurs at considerably lower temperatures and leads to hydrocarbon mixtures with higher commercial value, and it especially yields a much narrower product distribution of carbon atom number with a peak at lighter hydrocarbons [10, 11]. The different acid solids, zeolites (microporous materials) are one of the preferred catalysts for the conversion of plastic wastes. However, their pore sizes restrict the access of bulky molecules to acid sites located inside the channels. This fact can be overcome by using large pore size catalysts, which would allow a better accessibility to the internal acid sites.

Among plastic materials, PE world production in 1997, are reached 33 million tons, accounting for 70% of polyolefins consumption and 44% among all thermoplastic materials. Previous studies of the catalytic cracking of PE, which constitutes about 47 wt% of the total plastic waste in the United States, have shown that the molecular weight range of products are generated by heating this polymer and can be greatly restricted with solid acid catalysts. Different works have been published using solid-acid catalysts mainly amorphous $SiO_2-Al_2O_3$, different types of

zeolites [12, 13] and mesoporous materials [14, 15]. Thus, some of the studies reported in the literature will be reviewed below.

1.2 Literature reviews

Garforth *et al.* [16] reported that zeolite Y and ZSM-5 accelerated the degradation of HDPE by reducing the activation energy of the reaction. In addition, ZSM-5 exhibited lower coke deposits compare to zeolite Y. The narrow pore openings and no supercages of ZSM-5 inhibited the bulky molecules to access the internal active site and the bimolecular processed to take place inside the channels. The bulky molecules initially degraded on the outer surface and smaller cracked products may enter to the channels. Thus, the different product selectivity was obtained due to the different pore system. In large pore zeolite Y, alkenes rapidly undergo bimolecular hydrogen transferred to produce alkanes, thus zeolite Y mainly yielded alkanes with less alkenes and aromatics; whereas ZSM-5 gave alkenes as primary product. The n-HZSM-5 with nanometer crystal size was reported to be an effective catalyst for enhancing degradation of polyolefin. The high external surface area promoted the cracking activity and gave rise in C_1–C_4 gaseous hydrocarbon products whereas H-Beta produced more liquids in the range of C_5–C_{12}. Conversely, mesoporous HMCM-41 yielded high fractions of both C_5–C_{12} and C_{12}–C_{30} liquid hydrocarbons.

In 1998, Uddin *et al.* [17] reported the degradation of PE and PP over non-acidic hexagonal mesoporous silica–FSM-16 and solid acid catalysts such as silica–alumina, ZSM-5, silicalite and silica gel with thermal degradation. ZSM-5 produced more gaseous products than other catalysts, whereas, mesoporous silica–FSM-16 accelerated the degradation rate and increased the liquid product yield, which mainly consisted of low molecular weight products. In contrast, silicalite and silica gel had less affect on polymer degradation.

Sakata *et al.* [18] reported that mesoporous silica (KFS-16/FSM-16), which possessed no acidic sites, exhibited a fast degradation rate of PE as silica–alumina (SA-1) at 430°C and produced more liquid product yield. Heavier waxy compounds were cracked into kerosene or diesel by the free radical flask concept related to the hexagonal structure of silica.

Aguado *et al.* [19] reported the efficiency of mesoporous aluminosilicate MCM-41 catalyst in degradation of polyolefins into liquid fuel. MCM-41 (Si/Al = 42) showed a good performance in PP cracking over silica–alumina (Si/Al = 35.6) and ZSM-5 (Si/Al = 31). The amount of liquid product obtained was high in the range of gasoline (C_5–C_{12}) and fair in the middle distillates (C_{13}–C_{22}), which suggested a correlation between pore size distribution of catalyst and product selectivity. On the contrary, MCM-41 (Si/Al = 42) exhibit low activity for degradation of HDPE and LDPE compared with ZSM-5, which was related to the strength of acid sites.

Serrano *et al.* [20] studied catalytic cracking of a polyolefin mixture consisting of polypropylene and both low- and high- density polyethylene at 400 °C over the different acid solids as catalyst, as well as those corresponding to a thermal cracking experiment used as the reference. The following activity order is observed:

n-HZSM-5 > HBeta > HMCM-41 > SiO_2-Al_2O_3 > HZSM-5 > HY > thermal conversion

The highest conversion was obtained with the HZSM-5 zeolite of small crystal size (n-HZSM-5) with a value of around 84%. Both HBeta zeolite and HMCM-41 showed also high conversions, 68 and 49%, respectively. On the contrary, the rest of the catalysts (SiO_2-Al_2O_3, HZSM-5, and HY) led to really low conversions that reach at best 10 wt % in the case of the amorphous SiO_2-Al_2O_3. In the case of n-HZSM-5, the presence of a high external surface area enhanced its cracking activity, because the zeolite external acid sites were not sterically hindered for the conversion of the bulky polyolefin molecules. Likewise, the high surface area and large pores presented in HMCM-41 were responsible for the high conversions. Significant differences were observed in the product distribution: n-HZSM-5 showed the highest selectivity toward C_1-C_4 gaseous hydrocarbons (50 wt %), HBeta led mainly to liquid hydrocarbons in the range C_5-C_{12} (60 wt %), whereas HMCM-41 yields both C_5-C_{12} (54 wt %) and C_{13}-C_{30} (32 wt %) fractions.

In 2000, Aguado *et al.* [1] investigated the catalytic degradation of polypropylene and both low- and high-density polyethylene over zeolite beta synthesized according to different procedures. Zeolite beta synthesized by the fluoride method had a low activity for the cracking of polyolefins, which was related to its large crystal size (12 mm), very small external surface area and poor aluminium incorporation. In contrast, zeolite beta synthesized from amorphous xerogels consisted

of small crystallites ($\leq$200 nm), high external surface areas and allowed all the polyolefins to be degraded with high conversion (40-60%) and good selectivity toward C_5-C_{12} hydrocarbons (60-70%), heavier products being hardly obtained (<6%). In the catalytic cracking of the three studied polyolefins over the beta zeolites having small crystal sizes [Al-beta(X) and Ti-Al-beta(X)], LDPE and PP had shown higher conversions than HDPE. This behavior was explained considering the presence of tertiary carbons in the structure of these two plastics that provided favourable positions for the initiation of the polymer chain cracking. The incorporation of titanium into the BEA structure had been proved to enhance the catalytic activity, as denoted by the highest conversion per Al atom obtained with the Ti-Al-beta sample compared to Al-beta.

Lin *et al.* [14] investigated the catalytic cracking of polypropylene using various catalysts including mesoporous material. Because of larger pore size and weaker acidity of MCM-41 as compared to zeolites. The results showed that MCM-41 gave the highest liquid yield and selectivity to gasoline up to 60.56% while zeolitic materials i.e. HUSY, HZSM-5 and HMOR were selectivity to gaseous product which less value.

Nanocrystalline HZSM-5 zeolite had demonstrated to be a successful catalyst in the degradation of polyolefins (HDPE, LDPE and PP) into light hydrocarbon mixtures. Choudhary *et al.* reported that the high activity and the high selectivity toward gases obtained over this catalyst could be explained as a consequence of two factors [22]: the strong acidity of the zeolite and the considerable amount of fully accessible acid sites located on the external surface of the nanocrystalline zeolite samples. Catalytic cracking over acid solids took place through the formation of carbenium and carbonium ions. The strength and nature (Brønsted or Lewis) of the acid sites affected both the activity and the products obtained in the cracking: the stronger the sites, the lighter hydrocarbon mixture obtained [23, 24]. However, due to the bulky nature of the polymer macromolecules, another factor playing a key role for catalyst activity is the accessibility of the acid sites. Thus, several works had been reported on the polymer cracking over mesoporous materials or nanosized zeolites. Although in some of the works the amount of external surface of the catalyst was considered as one of the main factors affecting the catalyst activity, the influence of this variable had not been studied as deeply as the strength of the acid sites [25].

Negelein *et al.* [26] and Manos *et al.* [27] reported the effects of catalyst acidity on cracking of plastics. The higher acidity of a catalyst obtained the higher amount of volatile products. Sulfated zirconia, a strong acid catalyst, lowered the cracking temperature and facilitated hydride abstraction mechanism, resulting in an increase in volatile saturated hydrocarbon products. Silica–alumina and HZSM-5 catalysts mainly produced olefins as primary volatile products. This was because the channels of HZSM-5 was restricted for carbenium ion rearrangements and facilitated formation of propene. Manos *et al.* [27] reported the effect of a polymer to catalyst ratio expressed in terms of acidity content on degradation of plastic waste using commercial catalyst—zeolite Y. A sharp increase in liquid hydrocarbon yield was observed at the acidity of 1–7% when compared with pure zeolite Y and after 7% acidity, liquid hydrocarbon yield exhibited a negative correlation to the acidity content.

Several studies had been conducted describing the cracking of pure polyolefins over different acid solids like zeolites clays and mesostructured materials. Differences in the catalytic activities of these solids had usually been related to their acid properties, primarily the strength and number of the acid sites. Textural properties, such as surface area, particle size and pore size distribution, had been reported to play a key role, as they controlled the accessibility of bulky plastic molecules to internal catalytically active sites. While most work on the catalytic cracking of plastics had been conducted using pure polymers, it was accepted that the degradation process might be affect by the presence of contaminants as well as by chemical alterations that took place in the polymeric structure during its use. Understanding the behavior of catalysts on waste polymeric plastics was essential to evaluate their potential application in commercial feedstock recycling processes.

The micropores of zeolites were often advantageous to induce shape selectivity, but enhance accessibility was frequently desirable in order to restrict deleterious mass transfer effects and to allow catalytic conversion of larger molecules. A recent approach, developed first by Corma and co-workers to enhance the accessibility was the delamination of the lamellar zeolites [28, 29, 40]. They had established that microporous lamellar zeolites could be treated to generate single crystalline sheets of zeolitic nature where all the potential active sites were accessible through the external surface. The lamellar zeolite, it was possibile to individuate a swellable intermediate state, in which a swelling agent was interposed between the

layers of the material before transforming it by calcinations into a non swellable final state having order in three dimensions [30]. In the swellable intermediate state, it was possible to interpose the swelling agent between the layers of the zeolitic material, and successively the swollen product was submitted to ultrasound treatments to promote the interlayer separation. The final calcination produced single layers of zeolitic materials.

The catalytic pyrolysis of plastic wastes permitted valuable products to be obtained similar to diesel and gasoline [31]. Several catalysts had been used, but zeolite and mesoporous materials were the most important because of their porous structure and acid properties. The more important disadvantage of these catalysts was the formation of heavy by-products which form a deposit on the surface (coke) and caused the gradual deactivation of the catalyst and also affected the product distribution and selectivity. The deactivation of zeolites in polymer cracking had been studied, and several papers had been reported. For example, Lin *et al.* [32] studied the deactivation of the USY zeolite during the catalytic pyrolysis of high density polyethylene.

Marcilla *et al.* [33] studied the deactivation of HZSM-5 and HUSY during the catalytic pyrolysis of polyethylene using a thermobalance, showing that as the HUSY zeolite presented a fast deactivation although small pore size in HZSM5 prevents coke deposition. These studied were focused on the catalytic activity of the zeolites and no information about the nature of the coke was reported. The knowledge of the nature of the coke was very important because this permitted information was obtained about the possible deactivation mechanism of the zeolite.

Several studies had been conducted describing the cracking of plastic over different acid solid catalysts such as zeolite, clays and mesoporous materials. However, no work had been reported on PP waste degradations over MCM-22 and del-MCM-22 catalysts.

1.3 Objectives

    1.3.1   To synthesize and characterize MCM-22 catalyst and study the effect of crystallization time and SiO_2/Al_2O_3 ratios.

    1.3.2   To study the optimum condition for delamination of MCM-22 (del-MCM-22) [36-39, 73].

    1.3.3   To study the effect of reaction temperature, polymer to catalyst ratio, and SiO_2/Al_2O_3 ratio of catalyst in catalytic cracking of polypropylene over MCM-22.

    1.3.4   To investigate the efficiency, stability of del-MCM-22 for cracking of polypropylene waste.

1.4 Scope of work

Synthesis MCM-22 [34, 35] by hydrothermal method is investigated using hexamethyleneimine (HMI) as directing agent. The SiO_2/Al_2O_3 molar ratios in gel or reactant mixture are varied from 30 to 400. The optimum condition for cracking of polypropylene over MCM-22 is determined by studying the effects of treatment routes for ion exchange, temperatures, catalyst amounts and SiO_2/Al_2O_3 ratios. They are tested for their activity in the catalytic cracking of polypropylene waste under optimum condition.