CHAPTER I

INTRODUCTION

Plastics have become essential materials due to their numerous applications in normal life. The worldwide production of plastics has increased from around 5 million tones in the 1950s to nearly 100 million tones today. Plastics have been one of the materials with the fastest growth because of their wide range of application (Figure 1.1).
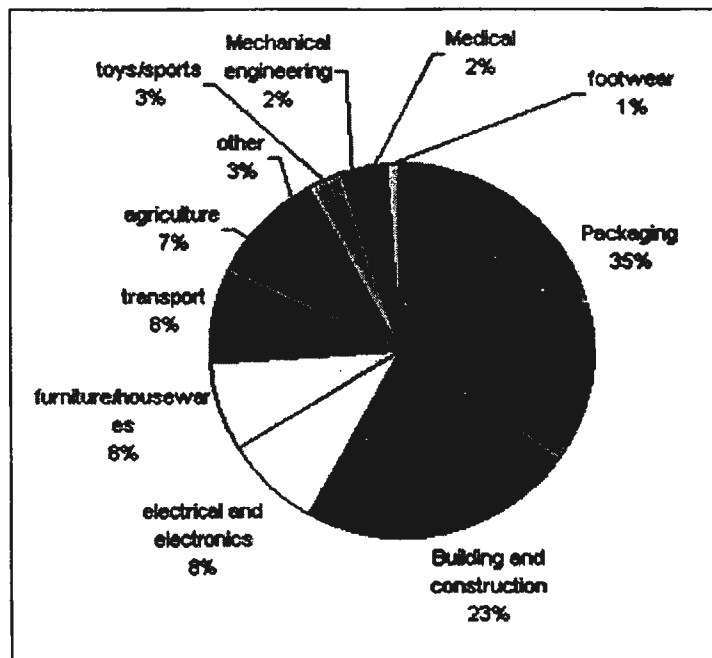

Figure 1.1 Plastic applications. [1]

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.

Plastic [2, 3]

The considerable growth in plastic use is due to the beneficial properties of plastics. These include:

- Extreme versatility and ability to be tailored to meet very specific technical needs.
- Lighter weight than competing materials, reducing fuel consumption during transportation.
- 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.

There are about 50 different groups of plastics, with hundreds of different varieties. All types of plastic are recyclable. To make sorting and thus recycling easier, the American Society of Plastics Industry developed a standard marking code to help consumers identify and sort the main types of plastic. These types and their most common uses are presented in Table1.1.

Table 1.1 Commodity Plastics and Their Uses [4]

Type	Abbreviation	Major Uses
⟨1⟩	PET	**Polyethylene terephthalate** - Fizzy drink bottles and oven-ready meal trays.
⟨2⟩	HDPE	**High-density polyethylene** - Bottles for milk and washing-up liquids.
⟨3⟩	PVC	**Polyvinyl chloride** - Food trays, cling film, bottles for squash, mineral water and shampoo.
⟨4⟩	LDPE	**Low density polyethylene** - Carrier bags and bin liners.
⟨5⟩	PP	**Polypropylene** - Margarine tubs, microwaveable meal trays.
⟨6⟩	PS	**Polystyrene** - Yoghurt pots, foam meat or fish trays, hamburger boxes and egg cartons, vending cups, plastic cutlery, protective packaging for electronic goods and toys.
⟨7⟩	OTHER	**Any other plastics** that do not fall into any of the above categories. - An example is melamine, which is often used in plastic plates and cups.

The global plastic consumption in Western Europe in 1997 was 3507 million tones and it is expected to grow 4 % annually until 2006. Unfortunately, such high consumption levels are accompanied by the generation of large amounts of post-use plastic wastes that account approximately for a 65 % of the plastic production. An average weight composition of the different type of plastics present in Western Europe is shown in Figure 1.2.
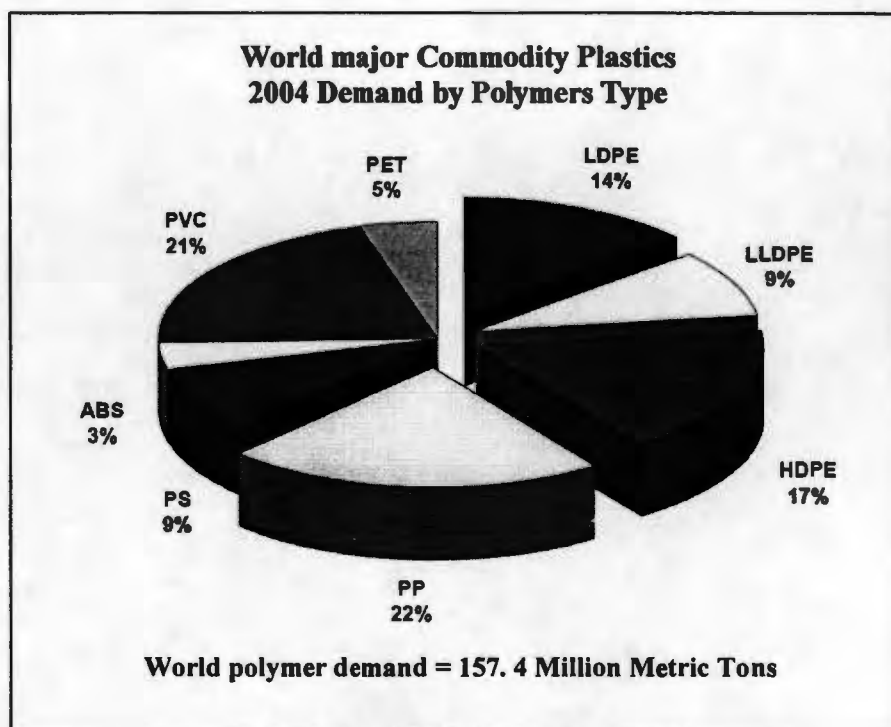
Figure 1.2 World major commodity plastics 2004 demand by polymers type. [5]

Feedstock recycling of polyolefins into short-chain hydrocarbons has been widely investigated in recent years [6]. Polyethylene (PE) and polypropylene (PP) account for about 62 wt % of total plastics household wastes, and in contrast with other thermoplastics such as polystyrene (PS) or polyethylene terephthalate (PET), thermal degradation proceeds with low yields into the corresponding raw monomers [7, 8]. Moreover, thermal conversion of PE and PP leads to a wide product distribution with poor economical value, which should be further upgraded [9].

Polyethylene is by far the world's most used plastic (about 39% of the plastics used in 2004 were polyethylene and its consumption is constantly growing). Polyethylene can be found in the market in several grades: [10]

1. Low density polyethylene (LDPE), is an ethylene homopolymer produced in a high pressure uncatalyzed process, which contains long and short branches; these branches in LDPE prevent a good packing of polymer molecules and in consequence the polymer melts at low temperatures.

2. High density polyethylene (HDPE), was firstly obtained in 1958 by the use of Phillips and Ziegler-Natta catalysts. This grade, which consists in unbranched

polyethylene molecular chains, has a higher melting temperature, but also a higher fragility.

3. Linear low density polyethylene (LLDPE), was produced in the 1980s by copolymerization of ethylene with other olefins like 1-hexene. Thus, a great quantity of short branches was added to the main polyethylene chain, achieving intermediate properties between HDPE and LDPE.

As can be seen in Figure 1.2, PE and PP are major consumed plastic wastes. Municipal and industrial plastic wastes are treated predominantly in three ways, by landfill, incineration and recycling. In 2001 Environment report, 80% of post-consumer plastic waste is sent to landfill, 8% is incineration and only 7% is recycled. However, each of these methods has disadvantages. Landfill treatment and of plastic waste are less desirable due to high cost, poor biodegradability and the possibility of unacceptable emission. Recycling is a popular recovery path but recycled plastic product often costs more than virgin plastic. [11, 12]

An alternative strategy is that of chemical recycling, which has attracted much interest recently with the aim of converting waste polymers 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 degradation of waste plastic. [13]

1. Thermal degradation produces a broad product range and required high operating temperature, typically more than 500°C and even up to 900°C.

2. Catalytic degradation might provide control the product distribution and reducing the reaction temperature.

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. [14, 15]

Among plastic materials, PE world production in 1997 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 generated by heating

this polymer can be greatly restricted with solid acid catalysts. Different works have been published using solid-acid catalysts mainly amorphous $SiO_2-Al_2O_3$ and different types of zeolites [16, 17]. Thus, some of the studies reported in the literature will be reviewed below.

D.P. Serrano *et al.* [18] reported about the catalytic cracking of PS over HMCM-41, HZSM-5 and amorphous $SiO_2-Al_2O_3$ at 375°C. The highest catalytic activity is obtained over HMCM-41(~35%), with a value close to the thermal cracking (~36%). However, the other two materials conversions were roughly half of the one obtained in the thermal treatment (18.0 and 18.6%, respectively). This fact has been explained by the existence of competitive cross-linking reaction promoted by the acid catalysts. Two types of behavior can be clearly distinguished according to the product distribution. Styrene was the major product in both thermal and catalytic cracking over the HZSM-5 zeolite. Silica-alumina and HMCM-41 mainly result in formation of benzene and ethyl benzene. Moreover, the higher the acid strength of the catalyst, the larger the extension of the cross-linking process, which explains the low cracking activity observed over the HZSM-5 zeolite.

R.A. Garcia *et al.* [19] have investigated and compared the behavior of hybrid ZSM-5/MCM-41 materials with pure Al-MCM-41 and HZSM-5 samples for catalytic cracking of HDPE. The samples obtained exhibited remarkable catalytic activity in the HDPE cracking despite the low temperature (380°C) and catalyst loadings used (plastic/catalyst mass ratio=100), leading to polyolefin conversions higher than both Al-MCM-41 and HZSM-5. Light hydrocarbons with a narrow product distribution and rich in olefins (C_3-C_5) are the main components obtained over the hybrid and HZSM-5 catalyst. The superior catalytic activity of the hybrid materials for the HDPE cracking in regards to the Al-MCM-41 and pure HZSM-5 samples have been assigned to a right combination of acid strength and accessibility of the acid sites.

In addition, Y.-H. Lin *et al.* [20] have studied catalytic cracking of HDPE over various catalysts using a fluidized-bed reactor operating isothermally at ambient pressure. The reaction temperature was 360°C. HZSM-5 catalyzed cracking resulted in much larger amounts of volatile hydrocarbons compared with cracking over MCM-41 and $SiO_2-Al_2O_3$ (SAHA). When an HZSM-5 was used as a cracking addition in combination with MCM-41 and SAHA, the solid mixed catalysts produced less gas with a lower loss of gasoline than HZSM-5. MCM-41with large mesopores and

SAHA with weaker acid sites resulted in a highly olefinic product and gave rise to the broadest carbon range of C_3-C_7. In HDPE cracking over MCM-41 at temperatures in the range of 290°C-430°C, the liquid and residue fractions decreased with increasing reaction temperature. Both SAHA and MCM-41 materials allow bulky reactions to occurred leading to the generation of coke and subsequently deactivation of the catalyst.

George Manos *et al.* [21] explored the catalytic cracking of HDPE over ultrastable Y, Y, β zeolites, mordenite and ZSM-5 at 360°C. The structure of the zeolite framework has shown a significant influence on the product distribution. Over large-pore USY, Y and β zeolites, alkanes were the main products with less amounts of alkenes and aromatics and only very small amounts of cycloalkanes and cycloalkenes. Medium-pore mordenite and ZSM-5 gave alkenes as major products. The hydrocarbons formed with medium-pore zeolites were lighter than those formed with large-pore zeolites. A similar order was found regarding the bond saturation:

(more alkenes) ZSM-5<mordenite<β<Y<USY (more alkanes)

Sami A.I. Barri *et al.* [22] described the catalytic cracking of PE over all-silica MCM-41. Synthesis of MCM-41 using microwave heating produces samples with smaller unit cell parameters than that crystallized using conventional heating. The cracking activity increases with the degree of crystallinity of the catalyst. MCM-41 with small pore diameter gave higher activity than that with large pore diameter. The product distribution indicated a carbenium ion mechanism. The levels of isobutene and isobutane are very high relative to the levels of C_1 and C_2 as compared with the non-catalytic test runs. The adsorption of PE on the surface of the channels increases the basicity of the hydrocarbon fragment and promotes the protonation reaction by the silanol groups and stabilizes the formation of carbenium ions, as shown in Scheme 1.1.

Wall of MCM-41 channel

Polyethylenic fragment
or molecule
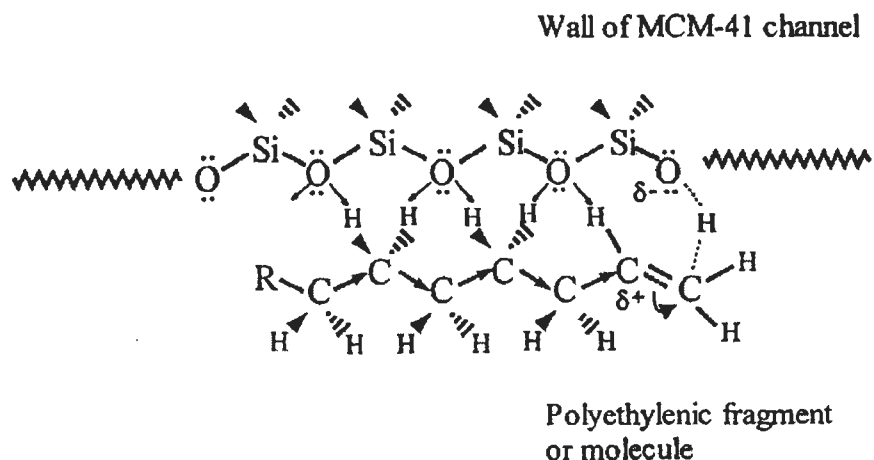
Scheme1.1 The interaction of hydrocarbon fragment and silanol group.

A. Garforth *et al.* [23] studied the catalytic cracking of HDPE using H-Y zeolite, HZSM-5, silica-alumina (SAHA) and pure and aluminum MCM-41 as catalysts. Thermogravimetric analysis has been used to investigate the activity of various catalysts. SAHA (130 KJ/mol) significantly reduced the activation energy as compared with thermal processes (250-305 KJ/mol). H-Y and HZSM-5 (95-110 KJ/mol) further reduced the activation energy resulting in more rapid degradation. Al-MCM-41(80 KJ/mol) was found to be active in the cracking of HDPE at a rate similar to that of HZSM-5. Activation energy order was as follow:

MCM-41(Al)> zeolites(ZSM-5, Y)> SAHA> MCM-41(Si)
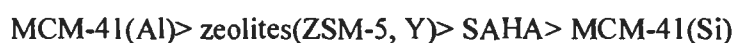
The results confirm these new mesoporous materials MCM-41 containing aluminum were active in the cracking of polyolefins.

D.P. Serrano *et al.* [24,25] described the conversion of LDPE using a continuous screw kiln reactor provided with two zones of reaction temperature. In thermal cracking, LDPE is completely degraded when the temperature in the second zone reaches 500°C. The main products obtained are gasoline (25% selectivity) and linear paraffins and α-olefins (55-60% selectivity). Catalytic LDPE cracking over a MCM-41 type catalyst proceeds in the screw kiln reactor with high conversions for reaction temperatures around 450°C. In this case, gasolines are preferentially produced with selectivities up to 80%. Moreover, high amounts of C_7 and C_8

hydrocarbons are present in the gasoline fractions, which are assigned to catalytic oligomerization reactions that selectively affect to C_3 and C_4 gashouse hydrocarbons.

Recently, J. Aguado et al. [26] investigated the catalytic conversion of LDPE, HDPE and PP using Al-MCM-41, ZSM-5 and amorphous silica-alumina as catalyst. The catalytic cracking of HDPE and LDPE was investigated at 400°C in a batch reactor with duration of the experiments of 30 min. In the catalytic cracking of HDPE and LDPE, the highest activity was observed with ZSM-5 due to its stronger acidity. But in the catalytic conversion of PP, the Al-MCM-41sample led to almost 100% conversion whereas the activity obtained with the ZSM-5 was very close to that of thermal cracking (11.3%). Moreover, for the cracking of LDPE, HDPE and PP, the selectivities toward hydrocarbons in the range of gasolines and middle distillates obtained over MCM-41 are clearly higher than those of ZSM-5. Therefore, MCM-41 was a potential catalyst for the conversion of polyolefinic plastic waste into liquid fuels.

Y. Sakata et al. [27] reported about catalytic cracking of PE and PP using FSM, silica-alumina, ZSM-5, silicalite and silica-gel as catalyst by batch operation at 430°C and 380°C. Compared with thermal degradation, FSM catalyst accelerated the initial rate of degradation, increased the liquid product yield and promoted degradation into lower molecular weight products. Silicalite and silica-gel had very negligible effects on polymer degradation. When the batch reaction was repeated four times using FSM catalyst, the extent of the decline in the degradation rate was lower for PE than PP. Compared with the silica-alumina and ZSM-5, which turned completely black in the case of both PE and PP, the deposition of coke on the used FSM catalyst was extremely slight. It seems likely that catalytic effect of FSM for polyolefinic polymer degradation is related more to the hexagonal pore structure system of FSM.

In 2001, R. Van Grieken et al. [28] have studied thermal and catalytic cracking of PE under mild conditions. The catalysts employed were n-HZSM-5, HY zeolite, amorphous silica-alumina, activated carbon, Pd charcoal and MCM-41. Thermal cracking between 360°C and 420°C led to the highest solid yields. LDPE cracking was enhanced when catalyst was used, lowering the solid yield although in the case of MCM-41. The high BET surface area, uniform mesoporosity and medium acid strength of MCM-41 promoted the polymer cracking according to a random

scission mechanism, as well as, the hydrogen transfer reactions which reduced the olefinic character of the solid product. The use of HDPE instead of LDPE yielded a solid with a higher homogeneity, improving the properties of the waxy product for potential applications.

D.P. Serrano *et al.* [29] reported the catalytic cracking of polyolefin mixture consisting of 46.5 wt% LDPE, 25 wt% HDPE and 28.5 wt% PP at 400°C over a variety of acid solids as catalysts. The activity order was found as follow:

n-HZSM-5>H beta>HMCM-41>>SiO$_2$-Al$_2$O$_3$>HZSM-5>HY>thermal degradation

The activity order found for the different catalysts was related to their respective properties and the nature of the polyolefin mixture. HMCM-41 also leads to a high conversion because of its large pore size, which promotes the access of the polymer molecules to the acid sites. In the case of n-HZSM-5 and H-beta, the presence of a high external surface area enhances its cracking activity, because the external acid sites are not sterically hindered for the conversion of the bulky polyolefin molecules. Significant differences are observed in the product distribution: n-HZSM-5 shows the highest selectivity toward C$_{1-4}$(50 wt %), H beta leads mainly to liquid hydrocarbon C$_{5-12}$(60 wt %), whereas HMCM-41 yields both C$_{5-12}$(54 wt %) and C$_{13-30}$(32 wt %) fractions. Regarding the selectivity by carbon atom number, in all cases C$_4$ fraction was the major products, although its value changes widely depending on the catalyst.

From the previous works, the approach has demonstrated to be successful in the catalytic cracking of polyolefin over Al-MCM-41, which is a material of uniform mesoporosity. The large pore size, high surface area and moderate acid strength distribution of this catalyst allow plastic wastes to be degraded with high activity. The obtained products were controlled by pore size, acid strength, and particle size of the catalyst. This work intends to develop method for synthesis of Al-MCM-41 with different Si/Al ratios in gel and use in catalytic cracking of high density polyethylene and polypropylene wastes. Moreover, this catalyst was selected in order to study the influence of silica source, crystallization time, Si/Al ratios of the catalyst and optimal condition of NH$_4$Cl treatment to improve the activity and product distribution in the conversion of the high density polyethylene and polypropylene wastes.

Objectives

1. To synthesize Al-MCM-41 catalyst and study the effect of SiO_2-source, Si/Al ratios, and crystallization time.
2. To study the optimal condition for NH_4Cl treatment of Al-MCM-41.
3. To investigate the efficiency and stability of Al-MCM-41 for cracking of high density polyethylene and polypropylene wastes.
4. To study activity of regenerated Al-MCM-41 catalyst.