

CHAPTER I

INTRODUCTION

The growth of welfare levels in modern societies during the past decades has brought about a huge increase in the production of all kinds of commodities. Plastics have been one of the materials with the fastest growth because of their wide range of applications: household, agriculture, construction, packaging, etc. In the 1980s the total volume of plastics consumed worldwide overtook those of iron and steel. There are some economic reasons for the increasing use of plastics. They weigh less and are generally more corrosion resistant than metals. Like metals they are blended (alloyed) to improve their properties. Furthermore, plastics can be manufactured and processed with lower energy input than either metals or glass.

Plastics are divided into two major categories on the basis of economic considerations and end use: commodity and engineering. Commodity plastics are characterized by high volume and low cost; they may be compared with steel and aluminum in the metal industries. They are used frequently in the form of disposable items such as packaging film, but also find application in durable goods. Engineering plastics are higher in cost and much lower in volume but have superior mechanical properties and greater durability. They compete with metals, ceramics, and glass in a variety of applications.

Commodity plastics consist principally of four major thermoplastic polymers: polyethylene, polypropylene, poly(vinyl chloride), and polystyrene as shown in Table 1.1. Polyethylene is divided into low-density ($<0.94 \text{ g/cm}^3$) and high-density ($>0.94 \text{ g/cm}^3$) products. The difference in densities arises from structure: high-density polyethylene

(HDPE) is essentially a linear polymer, and low-density polyethylene (LDPE) is branched.¹ Polypropylene (PP) is the lightest major plastic, with a density of 0.90 g/cm³. PP can be made in isotactic, syndiotactic, or atactic form. The crystallizability of isotactic polypropylene makes it the sole form with properties of commercial interest. Isotactic polypropylene² is an essentially linear, highly crystalline polymer, with a melting point of 165°C. Commodity plastics represent about 90% of all thermoplastic production.

Table 1.1 Commodity Plastics and Their Uses¹

Type	Abbreviation	Major Uses
Low-density polyethylene	LDPE	Packaging film, wire and cable insulation, coatings
High-density polyethylene	HDPE	Bottles, drums, pipe, conduit, sheet
Polypropylene	PP	Automobile and appliance parts
Poly(vinyl chloride)	PVC	Construction, rigid pipe, flooring, wire
Polystyrene	PS	Packaging (foam and film), appliances

Waste disposal would be a problem even if the amount of waste per person stayed constant over the years. However, an increased standard of living and other changes in living style have aggravated the situation. In the United States, the population increased from 180 million in 1960 to 250 million in 1990, an increase of 39%. In the same period, municipal solid waste (MSW) increased³ at a faster rate so that the total waste per person increased by 62% as shown in Table 1.2. On the other hand, the per-capita generation of waste remained about the same from 1990 to 1993 and was projected to decrease slightly in the 1994-2000 period. MSW includes material from commercial, industrial, and institutional sources as well as residences.

Construction and demolition wastes are not included, nor is sludge from sewage treatment.

Table 1.2 Selected data on waste generation (million tons)³

Municipal Solid Waste Generation					
Item	1960	1970	1980	1990	1993
Paper products	30.0	44.0	55.0	73.0	77.8
Ferrous metals	10.0	13.0	12.0	12.0	12.9
Aluminum	0.4	0.8	1.8	2.7	3.0
Other nonferrous metals	0.2	0.7	1.1	1.2	1.2
Glass	6.7	12.7	15.0	13.0	13.7
Plastics	0.4	3.1	7.9	16.2	19.3
Rubber and leather	2.0	3.2	4.2	4.7	6.2
Textiles	1.7	2.0	2.6	5.7	6.1
Wood	3.0	4.0	6.7	12.3	13.7
Food wastes	12.2	12.8	13.2	13.1	13.8
Yard wastes	20.0	23.2	27.6	35.0	32.8
Waste, total	88.0	122.0	152.0	196.0	206.9
Other wastes	1.4	2.7	5.1	6.1	6.4

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In 1960 almost all solid waste was dumped or buried in landfills or incinerated. Plastics were easy to discard in the good old days, i.e. they were put into a landfill like many other old materials. The increasing amount of plastics (although still small in percentage terms), results in the growing demand for more land for landfills and the groundwater contamination by landfills. But open dumps are breeding grounds for rats and other carriers of pestilence and plastics scarcely add to groundwater contamination since polymers do not dissolve or degrade in landfills and are also not resorbed by organisms. Low molar mass additives which may be dissolved or resorbed have long been regulated for toxicological and/or ecological reasons; their diffusion is very slow. Most polymers cannot degrade naturally by light, oxygen, water, microorganisms, etc., because of their carbon chains and the lack of chromophores.⁴

The whole output of plastics in Western Europe in 1996 was estimated around 25.9 million tons, whereas the amount of plastic wastes collected in the same year was close to 16.9 million tons. The main source of plastic wastes in Western Europe is the municipal solid wastes (MSW) (63.3 wt%), followed by distribution and large industry (19.5 wt%). Plastics contained in MSW represent 8% of the total waste by weight and goes up to 20% when considered in volume. An average weight composition of the different type of plastics present in MSW in Western Europe⁵ is shown in Table 1.3.

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Table 1.3 Average weight composition of plastics in MSW in Western Europe.⁵

Type of plastic	Weight %
High density polyethylene (HDPE)	17.8
Low density polyethylene (LDPE)	22.7
Polypropylene (PP)	19.6
Polyvinyl chloride (PVC)	10.7
Polystyrene (PS)	11.9
Polyethylene terephthalate (PET)	8.1
Others	9.2

As can be seen in Table 1.3, PE and PP are major consumed plastic wastes, and this behavior constitutes a major problem. The preferred alternatives for the management of these wastes in Western Europe were deposition in landfills (75%) and incineration with energy recovery (14%), although these percentages change significantly from one country to another. Incineration is strongly questioned in many countries because of the possible emissions of different pollutants (dioxins, furans, etc.), which are toxic even at very low concentrations. On the other hand, the space available for landfills is decreasing progressively, whereas the deposition of plastic wastes there implies an undesired loss of raw materials due to the progressive depletion of natural resources.⁵⁻⁶

The global plastic consumption⁷ in Western Europe in 1997 was 35.7 million tons and it is expected to grow 4% annually until 2006. Unfortunately, such high consumption levels are accompanied by the generation of large amounts of used plastic wastes that account approximately for a 65% of the plastic production. The current situation in Western Europe is characterized by 70% landfilling, 15% energy recovery and 15% recycling (12% mechanical and 3% feedstock), which does not correspond with the self-sustainable model that rules modern waste management

strategies, and therefore great efforts are made in order to improve plastics recycling routes.

The U. S. alone is expected to generate about 172 million tons⁸ of municipal solid waste by the year 2000. Most of this waste currently goes to landfills. About 21% of the waste volume is made up of waste polymers, although only about 11% by weight. Hence, of the nearly 30 million tons/year of plastics produced in the U. S., over two-thirds will find its way into landfills. About one-quarter of this is single-use packaging material. However, over the last decade, more than 40% of the landfill sites in North America have been closed, and the rest are rapidly being filled. Despite the apparent need, there is great resistance in most communities in the U. S. and Canada to the establishment of new landfill sites.

In the past years, the increase in plastic materials consumption has led to a parallel rise in the generation of plastic wastes. The huge amount of waste plastics gives rise to serious environmental concerns. Different alternatives are currently being considered for reducing the environmental impact of plastic wastes. They are predominantly disposed of in landfill or subjected to incineration. Subsequently, the destruction of wastes by landfill is also undesirable due to high costs, poor biodegradability, and the available space in landfills is decreasing. Incineration of the plastics to recover energy produces toxic gaseous compounds and only shifts waste problem to one of air pollution. In many countries incineration of plastic waste is forbidden or politically unacceptable.⁹⁻¹⁶ During the past few years another alternative would be true recycling of plastics. Polymer recycling methods can be grouped as follows:

(1) Mechanical reprocessing of the used plastics to form new products. This method has found very limited application, as it is not generally applicable, because of the low quality of the new products and the need for pure waste plastic streams.

(2) Thermal and/or catalytic degradation of plastic waste to gas and liquid products, which can be utilized as fuels or chemicals. These methods seem to be the

most promising to be developed into a cost-effective commercial polymer recycling process to solve the acute environmental problem of plastic waste disposal.¹⁷⁻¹⁹

Because pure thermal degradation demands relatively high temperatures and its products required further processing for their quality to be upgraded because thermal conversion leads to a wide product distribution with poor economical value.^{10-11,20-21}

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.^{11,15}

Among plastic materials, PE world production in 1997 reached 33 million tons, accounting for 70% of polyolefins consumption and 44% among all thermoplastic materials.²² 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.²³ Different works have been published using solid-acid catalysts mainly amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$ and different types of zeolites. Thus, some of the studies reported in the literature will be reviewed below.

V. J. Fernandes, Jr. *et al.*²⁴ reported that thermal degradation of HDPE without catalyst gave rise to products distributed over a wide range of carbon atom numbers ($\text{C}_5\text{-C}_{26}$), the main fraction was $\text{C}_{10}\text{-C}_{15}$ (60.2%). The catalytic reaction led to lighter products ($\text{C}_5\text{-C}_{26}$), predominantly $\text{C}_5\text{-C}_9$ (73.5%). This behavior may be due the strong acid sites of the ZSM-5 zeolite, which can promote the polymer chains cracking.

D. P. Serrano *et al.*²⁵ have studied the catalytic degradation of polymeric over a silica-alumina catalyst at about 400°C. It was found that amorphous silica-alumina was the less active catalyst, which led to conversion just slightly higher than those observed by thermal cracking. This poor activity is probably originated by the weak acidity, the low surface area and a wide distribution of pore radius present in this

material. In recent works, they have shown that these problems can be overcome with the use of zeolitic materials as catalysts for the catalytic degradation process, since they have advantages in terms of pore sites distribution and acid strength.

The effects of aluminum content in solid-acid catalysts were examined with a comparison of the effectiveness of ZSM-5 ($\text{Si/Al} = 17.5$) and silicalite ($\text{Si/Al} > 1000$) catalyst, which has the same structure in catalytic cracking of PE. P. N. Sharratt *et al.*²⁶ reported that ZSM-5-catalyzed degradation resulted in much greater amounts of volatile hydrocarbons compared with degradation over silicalite. In the presence of the ZSM-5 catalyst at 360°C conversion to volatile hydrocarbons was more than 90 wt% of feed in 15 min, while silicalite yielded less than 6 wt% of feed after 60 min. It indicated that number of acid sites were controlled by aluminum content because Brønsted acid depends on aluminum content in the zeolite framework as shown in Figure 1.1.

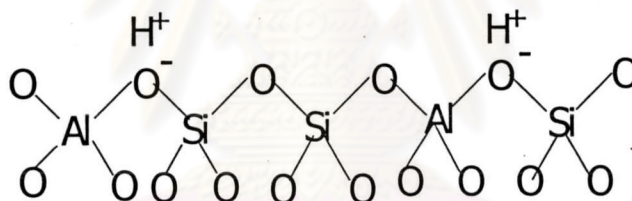


Figure 1.1 Zeolite framework

In addition, A. A. Garforth *et al.*²⁷⁻²⁸ reported about the PE cracking in a laboratory fluidized-bed reactor over ZSM-5 and amorphous silica-alumina catalysts at 360°C . It was found that amorphous silica-alumina showed the lowest conversion (84%) and generated an olefin-rich product, predominantly between $\text{C}_3\text{-C}_8$, whereas greater product selectivity was observed with ZSM-5 and Mordenite (MOR) as catalysts with over 80% of the product in the $\text{C}_3\text{-C}_5$ range and MOR generating the highest yield of C_4 for all catalysts studied.

Y. Uemichi *et al.*²⁹⁻³⁰ have investigated the catalytic conversion of PE in a fixed-bed flow reactor system using various catalysts. Zeolite ZSM-5 was very active for the carbon-carbon bond scission to yield gaseous products (C_1 - C_4) selectively. High selectivity to liquid products were observed on MOR and silica-alumina catalysts. It's showed that the obtained products were controlled by type and pore size of the catalyst. Moreover, rapid deactivations of zeolites Y and MOR occurred because of they are well-known to have a larger pore than ZSM-5 which favor the formation of coke. Even if a little amount of coke is produced, it blocks the entrance of the pores, resulting in a decrease in the accessibility to the acid sites remaining intact in the pores. Whereas ZSM-5 exhibited no catalyst deactivation due to a very low deposition of coke on the catalyst surface and a tridimensional small-pore network of the zeolite would resist coke formation.

D. W. Park *et al.*³¹ reported about the catalytic degradation of PE in a fixed-bed reactor. Solid acid catalysts, silica-alumina, zeolites ZSM-5, and Y were screened for PE degradation in the range of 450°C. Compare with those obtained by thermal degradation, ZSM-5 catalysts produced a much greater amount of gaseous product than any other catalyst. The initially cracked fragments can diffuse through the pores of ZSM-5 and react further in the cavities created at the intersection of the two channels, yielding more gaseous products. Zeolite Y and silica-alumina are known to have larger pore sizes than ZSM-5. Thus, the zeolite Y, in comparison to the ZSM-5 catalyst, showed more residue after the degradation. The zeolite Y was easily deactivated by coke formation because it had relatively large supercages within its crystal. Silica-alumina, ZSM-5, and Y-type zeolite catalysts greatly accelerated the degradation of PE. The liquid products over all the catalysts contained a narrow distribution of carbon numbers, from C_5 to C_{13} . The relative yield of C_5 - C_{13} fraction of these catalysts was greater than 97%. Thermal degradation products were distributed over a wide range of carbon numbers, from C_3 to C_{26} or higher.

P. T. Williams *et al.*³² pyrolysed PE in a fixed-bed reactor over ZSM-5 and Y-type zeolite catalysts at 400-600°C. In the presence of both the Y zeolite and the ZSM-5 catalyst, the oil yield decreased with a consequent increase in the gas yield and formation of carbon on the catalyst. As the temperature of the catalyst was increased from 400 to 600°C there was a further decrease in oil yield and increase in gas yield. The influence of both catalysts was to markedly increase the yield of aromatic compounds in the derived pyrolysis oil with a further increase in aromatic content with increase in catalyst temperature. Comparison of the two catalysts showed that the ZSM-5 catalyst gave higher concentrations of gases than the Y-type zeolite catalyst but the zeolite Y produced much higher concentrations of aromatic compounds in the derived oils. The high yield of aromatic compounds with the Y-type zeolite compared to the ZSM-5 catalyst was attributed to the difference in pore size, surface acidity and surface area of the two catalysts. Whereas ZSM-5 exhibited no catalyst deactivation due to a very low deposition of coke on the catalyst surface. In the catalytic cracking of PE, the highest activity is observed with zeolite ZSM-5 due to its stronger acidity. However, it was observed that in a zeolite with strong acid strength the amount of coke accumulated decreased. Acid strength of the zeolite depends on the Si/Al ratio in catalyst. Furthermore, Brønsted acid sites are up to aluminum content but Lewis acid sites are up to silicon content in the catalyst with low aluminum content.³² From this result, the Si/Al ratio is the main factor to control the effectiveness of the catalyst.

Although a wide variety of acid catalysts have been employed to crack PE, zeolites have proven particularly effective. However, zeolite catalysts are microporous materials having a maximum pore size of roughly 0.75 nm, its pores are too small for the plastic molecules to gain access into the channels; hence the initial stages of cracking are supposed to take place over a small portion of the total acid sites (those located on the external zeolite surface or at the pore entrances). This fact is

responsible for the appearance of steric hindrances in the cracking of bulky polymeric molecules, as has been found in the catalytic cracking of polypropylene over zeolites. This problem can be solved using catalysts of larger pores. The synthesis of a new family of silicate/aluminosilicate mesoporous material designated as M41S was discovered by Beck *et al.* in 1992.³³⁻³⁴ MCM-41 is one of the members of this family, possesses the similar behavior to zeolites. Furthermore, the attracting worldwide interest in MCM-41 has begun since their first synthesis due to their potential as catalysts, adsorbents, and host matrices. These applications are a consequence of their unique structure, which exhibits a regular array of uniform pore openings, high surface area ($>1000 \text{ m}^2/\text{g}$) and large pore size (1.5-10 nm). However, the MCM-41 materials constructed with pure-silica framework are of limited use for various applications because of the lack of acid sites and ion-exchange capacity.

S. A. I. Barri *et al.*³⁵ reported the ability of the all-silica MCM-41 material in cracking PE at 450°C. The product distribution was compared with those obtained from thermal cracking tests. MCM-41 catalyst gave substantially higher yields in the gas (9.7%) and liquid (mainly C₄-C₈) fraction than in the case of the non-catalytic test (gas fraction 6.7%). The catalytic degradation of this polymer led mainly to liquid fractions (83.4%). The surface acidity of the all-silica MCM-41 is attributed to the presence of silanol groups. It indicated that the all-silica MCM-41 material is not the appropriate catalyst for catalytic cracking process. Much attention has therefore been devoted to substitution of aluminum in the silicate framework. Consequently, Al-MCM-41 is a potential catalyst for reactions involving bulky molecules. It exhibited interesting catalytic properties for the degradation of polyethylene and polypropylene, usually the major component of plastic wastes.

N. D. Hesse *et al.*²³ investigated the effect of the solid acid catalyst pore size and acidity on PE catalytic cracking were examined when the polymer was cracked with ZSM-5, zeolite Y and Al-MCM-41. Volatile-product distributions depended on the catalyst acidity and pore size. Small olefins (C₃-C₅) were the most abundant products

when ZSM-5 catalysts were employed for cracking PE. In contrast, cracking by Al-MCM-41 produced primarily olefins volatile products (C_4 - C_6). Al-MCM-41 had the fewest weaker acid sites and lacked stronger acid sites. The high olefin yield (86.7%) for the catalytic cracking of PE suggests that β -scission dominated PE cracking reactions for the sample. To a lesser degree (60.3%), olefins also dominated the volatile-product detected when PE was cracked by ZSM-5, which had significantly more acid sites and a larger fraction of stronger acid sites compared with Al-MCM-41.

J. Aguado *et al.*³⁶ reported the influence of the main operating variables (plastic/catalyst mass ratio and temperature) on the activity and product distribution obtained during the cracking of a polyolefin mixture over ZSM-5 (Si/Al = 23.9) and Al-MCM-41 (Si/Al = 45.2) catalysts. Both materials presented a high activity for the conversion of the polyolefin mixture, leading to almost total plastic conversion as the temperature was increased from 375 to 450°C or as the plastic/catalyst ratio was varied from 200 to 4. The product distributions obtained with these two catalysts were completely different, which was related to the prevailing cracking mechanism. The zeolite H-ZSM-5, with high external surface area and strong acid sites, promotes end-chain scission reactions of the polymers, leading to light hydrocarbons, with around 80-90% of the products in the range C_3 - C_6 . In contrast, heavier products (C_5 - C_{12} and C_{13} - C_{22}) were obtained over Al-MCM-41, with an overall selectivity toward gasoline and gasoil fractions of 90%, indicating that random scission reactions are predominant as a result of the large pores and mild acidity of this material.

Recently, D. P. Serrano *et al.*⁵ have studied the potential use of Al-MCM-41 materials for the catalytic conversion of polyolefin mixture into chemicals and hydrocarbon mixtures useful as feedstocks at 400°C. The polyolefin mixture consisted of 46.5 wt% LDPE, 25 wt% HDPE, and 28.5 wt% PP, a proportion very close to the one usually found in the mixed plastics present in municipal solid wastes (MSW).

The catalytic activity and product distribution obtained with this material in the conversion of polyolefinic plastic into feestocks were discussed by comparison to those corresponding to different catalysts as shown in Table 1.4.

Table 1.4 Properties of the catalysts.

Catalyst	n-HZSM-5	HZSM-5	Hbeta	HY	HMCM-41	SiO ₂ -Al ₂ O ₃
Si/Al	24	31	39	3	45	36
Pore size (nm)	0.55	0.55	0.64	0.74	2.4	2-12
BET surface area (m ² g ⁻¹)	430	361	613	583	1164	261
External surface area (m ² g ⁻¹)	81	7	25	9	73	-
Pore volume (cm ³ g ⁻¹)	0.48	0.18	0.35	0.26	0.79	0.97
Micropore volume (cm ³ g ⁻¹)	0.15	0.17	0.24	0.23	-	-
Crystal size (μm)	0.075	3	0.20	0.50	0.2-2	-
Acidity (mequiv of NH ₃ g ⁻¹)	0.38	0.52	0.32	0.37	0.22	0.24
T _{max} (°C)	462	470	422	300	338	302

Note n-HZSM-5 was the ZSM-5 with crystal size in the nanometer range.

The activity order was as follows:

n-HZSM-5 > Hbeta > HMCM-41 >> SiO₂-Al₂O₃ > 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. It must be taken into account that catalytic cracking over acid solids takes place through the formation of carbenium and carbonium ions, which requires the presence of strong acid sites. However, a direct correlation between the acid strength, shown in Table 1.4, and the measured activities was not observed. For example, despite presenting the highest content of strong acid sites according to the ammonia temperature programmed desorption (NH₃-TPD) measurements, HZSM-5 exhibited a very low conversion of the plastic mixture. On the contrary, a direct relationship was clearly observed between the activity and the

external surface area/crystal size of the zeolite samples, which confirmed that steric and/or internal diffusion hindrances were present for the catalytic cracking of the bulky polymer molecules. The catalysts having small crystals presented high external surface area. The external acid sites were not limited by steric or diffusional problems; hence, they were essential to promote the initial steps of the polyolefin cracking, which explained the high activity obtained over both zeolites n-HZSM-5 and Hbeta.

J. Aguado *et al.*³⁷ investigated the catalytic cracking of LDPE, HDPE, and PP using Al-MCM-41, ZSM-5, and amorphous silica-alumina as catalysts. The catalytic degradation of both HDPE and LDPE was investigated at 400°C in a batch reactor with a duration of the experiments of 30 min. The activity order was observed: ZSM-5 > Al-MCM-41 > silica-alumina. But in the catalytic conversion of PP, the Al-MCM-41 sample led to almost 100% conversion whereas the activity obtained with the zeolite ZSM-5 was very close to that of the thermal cracking (11.3%). With Al-MCM-41 and the amorphous silica-alumina the conversion of PP was faster than in the case of HDPE and LDPE, which was related to the existence of a high proportion of tertiary carbons in the former and the presence of the side-chain methyl groups increased the effective cross section of the PP molecules compared to the PE chains, which perhaps prevent their access to the active sites located within the zeolite pores.

From the previous works, the approach has demonstrated to be successful in the catalytic cracking of polypropylene 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 tries to develop method for synthesis of Al-MCM-41 with different Si/Al ratios in gel and use in catalytic degradation of polypropylene. Moreover, this catalyst was selected in order to study the influence of temperatures

and Si/Al ratios of the catalyst to improve the activity and product distribution in the conversion of the polypropylene.

Objectives

1. To study methodology for synthesis of mesoporous crystalline Al-MCM-41.
2. To investigate optimal condition for catalytic degradation of PP using Al-MCM-41 with various Si/Al ratios as catalyst.



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