CHAPTER I

INTRODUCTION

1.1   Background

Plastic, a type of synthetic polymers, has greatly affected our lifestyle. Many articles that were previously made from naturally occurring materials such as wood, cotton, wool, iron, aluminum, and glass are being replaced or partially substituted by synthetic polymer. Plastic poses certain favorable properties such as their light weight, corrosion resistance, toughness, and ease of handling. They are also less expensive. The major use of plastic is in the packaging field. Moreover, plastic is used to produce many articles such as thermal and electric insulation, optic fibers manufacture, and medical devices. Another important and growing market for plastic is the automotive field. Many automobile parts are now made of plastic; among the most used polymers are polystyrene, polypropylene, polycarbonate, and polyvinylchloride. These materials reduce the cost and the weight of the cars. As a result, gasoline consumption is also reduced. Therefore, the global plastic consumption in Western Europe in 1997 was 35.7 million tons and it is expected to grow 4% annually until 2006.

In Thailand, plastics came just after World War II, with the introduction of foreign plastic household items. The production of plastic in Thailand began in 1950 but did not start to grow until the 1970's. A key event in the development of Thailand's petrochemical industry occurred in 1981, when large reserves of natural gas were found in the eastern part of the Gulf of Thailand.

However, since that time the industry has maintained steady growth year after year. The processing industry is now well equipped with the most modern equipment and machinery and is able to tackle very intricate parts molding. Precision molding and sophisticated extrusion processes are becoming part of day-to-day factory operations, which differs from a few years ago when these processes were not possible in Thailand.

Plastics can be divided into two major categories that are

- Thermoplastic: linear, one-dimensional polymers which have strong intramolecular covalent bonds and weak intermolecular Van Der Waals bonds. At elevated temperature, it is easy to "melt" these bonds and have molecular chains readily slide past one another. These polymers are capable of flow at elevated temperatures, can be remolded into different forms and in general, are dissolvable. A thermoplastic, under the application of appropriate heat, can be melted into a "liquid" state. Examples of thermoplastic are polyethylene, polypropylene, polystyrene, etc.

Table 1.1 Thermoplastics and their uses [1]

Type	Abbreviation	Major Uses
Low-density polyethylene	LDPE	Packaging film, wire and cable insulation
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

- Thermosetting: there are crosslinks or chemical bonds between adjacent chains, produce the thermoset characteristic of shape retention on heating. Once the chemical reaction or polymerization is complete, the polymer becomes a hard, infusible, insoluble material which cannot be softened, melted or molded non-destructively. A good example of a thermosetting plastic is a two-part epoxy systems in which a resin and hardener (both in a viscous state) are mixed and within several minutes, the polymerization is complete resulting in a hard epoxy plastic.

In Thailand, polyethylene and polypropylene were consumed about 60% (Figure1) of all plastic. Polypropylene is expected to be a highest growth during this year (2005-2006) [2].
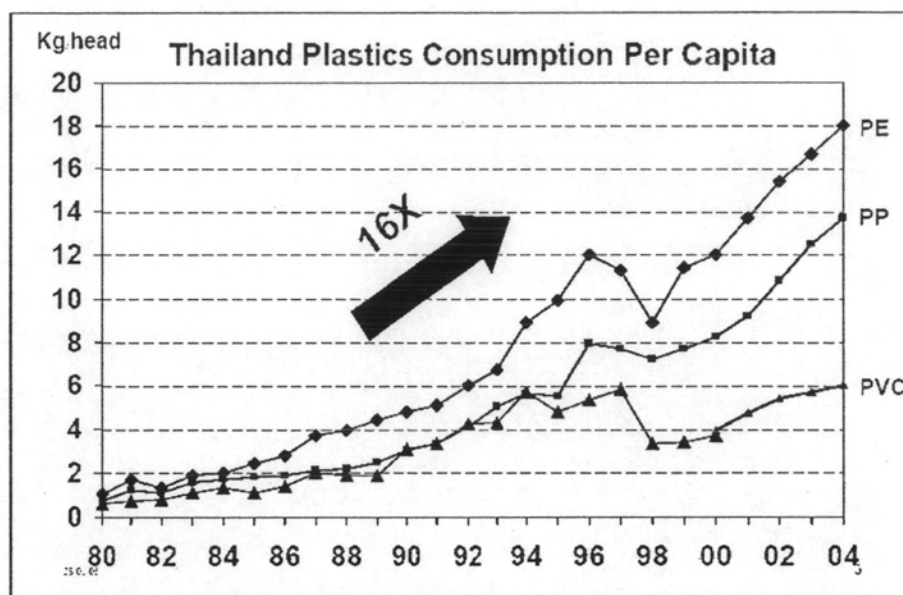
Figure 1.1: Thailand plastic consumption per capita in 1980-2004 [2].

The properties of commercial polypropylene are vary widely according to the percentage of crystalline isotactic polymer and the degree of polymerization. PP can be divided into three classes: homopolymer PP (isotactic PP); copolymer containing primarily PP (syndiotactic PP); and atactic PP. PP is composed of linear hydrocarbon chains and therefore its properties quite closely resemble those of PE. The properties of isotactic PP are particularly useful. The stereo regularity of macromolecule chain construction and the related high crystallinity give PP its outstanding characteristics. Currently, large scale commercially produced PP is up to 95% isotactic in nature. Homopolymer PP is one of the lightest thermoplastics, having a density ranging from $0.9 - 0.91$ g/cm^3. Pure isotactic PP has a melting temperature of 176°C with melting beginning around 140°C, which is much higher than PE. The chemical compatibility of PP is similar to that of HDPE. The tertiary carbon atoms reduce the chemical inertness of PP and make it above all more sensitive to oxidation. This sensitivity to oxidation must be compensated for by the addition of antioxidants.

Polypropylene possesses good water vapor barrier and fat resistance properties. PP is an excellent material for injection and extrusion process. The packaging containers, in particular bottles, made using this process should be mentioned. PP bottle maintain their shape well at high temperatures which allowed them to be hot filled. Injection molded container are used for frozen foods, e.g. ice cream. New PP packaging developments are multilayer bottles and can with inner

barrier layers which can be hot-filled or sterilized in an autoclave as well as directly steam sterilized.

Current statistics for Western Europe estimate a yearly plastic consumption of almost 100 kg per person, which account for over 39.7 million tones [3]. Unfortunately, plastic offer a serious problem in both resource problem (i.e. they are made from utilizing non rapidly renewable resources and their synthesis is typically energy demanding) and a disposal problem compose the large bulk by weight and by volume of what is termed solid waste. The management of such a vast waste stream represents not only a matter of environmental concern but also a source of commercial opportunities. The current situation in Europe, 62 wt% of all plastic residues are disposed of to landfill, which reduced from 70 wt% in 2004 [3], whereas incineration with energy recovery absorbs 23 wt%. Moreover, as mention above, landfilling and incineration does not correspond with the self-sustainable model that rules modern waste management strategies because of the decrease in space available for landfills and water pollution, while the incineration stimulate the unacceptable emissions such as NO_x, SO_x, CO_x, etc.

Nowadays, thermal and/or catalytic cracking 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 terms of accelerated depletion of natural resources. Moreover, as a result of limited petroleum problem as shown in Figure 1.2, the world's oil reserves was only 1293 billion barrels in 2006 [4], therefore, an interest in production of clean fuels for transport, e.g. biodiesel, gasoline is significantly increasing [5]. Furthermore, normally, cracking process is applied to refinery industries in order to produce a high capacity of light fraction of liquid hydrocarbon, i. e. gasoline. Due to the gasoline obtained by the direct distillation of crude petroleum is insufficient to meet demand, the additional gasoline is obtained by the cracking of higher boiling petroleum fractions. The reaction is carried out by heating the higher fraction, such as gas oil at 450- 550°C [3] in the presence of an aluminum silica type catalyst. To date, the catalytic cracking procedure was interested by many researchers to use in waste plastic cracking.
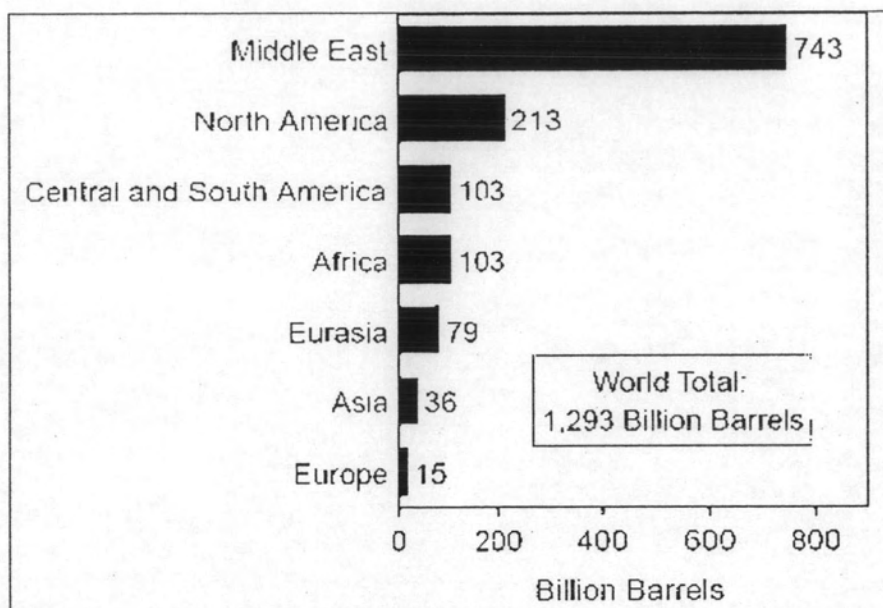
Figure 1.2   World proved oil reserves by geographic region, 2006 [4].

Previously, thermal cracking of waste plastic under different conditions has been well investigated by researchers. In case of waste plastic like HDPE, LDPE, and PP this process has been reported to proceed through a random scission mechanism that generates a wide range of product. In such a recycling process, the most valuable product is obviously liquid fuel. Although gaseous products are useful too, as their burning can contribute to the energy demand of an endothermic polymer cracking process, excess gas production is not desirable. Gaseous products are considered of low value because of their transportation costs. Consequently, the target of a commercially viable recycling process should be an increase of the liquid product yield. It was found that both the yields and chemical properties of products can be modified with catalysts due to:

1. Catalysts promote the degradation reaction to occur at lower temperature, with implies lower energy consumptions.

2. The most importantly, the shape selectivity exhibited by certain catalysts allows the formation of narrower distribution of products, which may be directed towards light fraction and aromatic hydrocarbon with higher market value.

Several studies have been conducted describing the cracking of plastic over different acid solids such as zeolites, clays and mesostructured materials. However,

there are only few papers reported about the synthesis of Al-SBA-15 for cracking of polypropylene waste.

1.2 Literature reviews

1.2.1 Cracking catalysts

The key reaction in catalytic cracking is the addition of proton (H^+) to form a positively charged ion. Any acid would do, but in a conventional chemical reaction of hydrocarbons with a strong acid (e.g., H_2SO_4), it would be kind of difficult both to separate out what we wanted afterward and avoid corroding cracking reactors. Thus, the catalysts used are solids with acidic surfaces, so they stay where they are put. Acid treated clays were the first catalyst used in catalytic cracking process [6], but have been replaced by synthetic silica-alumina, which is more active and stable. Incorporating zeolites crystalline alumina silica catalyst improved selectivity towards aromatics. These catalysts have both Lewis and Brønsted acid sites that promote carbonium ion formation. An important structure feather of zeolites is the presence of holes in crystal lattice, which are formed by silica tetrahedra as exhibited in Figure 1.3.
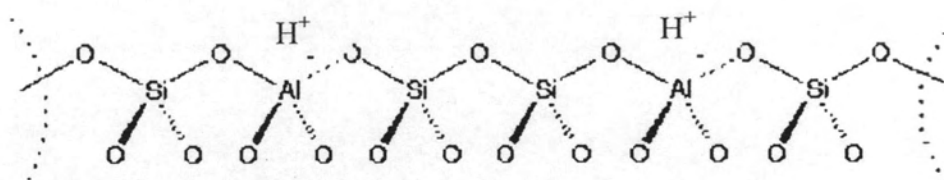

Figure 1.3   Framework of zeolite consisted of SiO_4 and $[AlO_4]^-$.

Zeolites as cracking catalysts are characterized by higher activity and better selectivity toward light fraction than amorphous silica-alumina catalysts. This is attributed to a greater acid sites and a higher adsorption power for the reactants on the catalyst surface. The higher selectivity of zeolites is attributed to its smaller pores which allow diffusion of only smaller molecules through their pores, and to the higher rate of hydrogen transfer reactions.

Deactivation of zeolites catalyst occurs due to coke formation and to poisoning by heavy metals. In general, there are two types of catalyst deactivation that occur in a catalytic cracking system, reversible and irreversible. Reversible

deactivation occurs due to coke deposition. This is reversed by burning coke in the generator. Irreversible deactivation result as a combination of four separate but interrelated mechanisms: zeolite dealumination, zeolite decomposition, matrix surface collapse and contamination e.g. by metal such as vanadium and sodium.

Since the discovery of surfactant-organized silicas and silicate in the early 1990s, there are extensive researches in this field. In discussing catalytic application, the relevant materials will probably be classified into three types by different synthetic procedures. The first one is that for M41s family of silica and aluminosilicates, *i. e.* hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50 produced by Mobil group [7]. Preparation of these synthetic materials involves ionic surfactants i.e. alkyltrimethyl ammonium (C_nTA^+, $8<n<18$) as a structure directing agents. Especially MCM-41, many researchers have focused on the study of it in term of industrial catalyst. Therefore, Inagaki *et al.* [8] reported the synthesis of a hexagonal mesoporous material namely FSM-16 (Folded Sheets Mesoporous Material) from a layer of polysilicate by using ionic surfactants, *i. e.* tertiary amine ($C_nH_{2n+1}N^+(CH_3)_3$) as a structure directing agent similar to that of MCM-41 preparation.

The second synthetic procedure was introduced by Pinnavania *et al.*[9] using two neutral routes based on hydrogen bonding and self assembly of non ionic primarily long chain alkyl amines surfactant (such as 1-dodecylamine). The hexagonal mesoporous silica, *i. e.* HMS and MSU produced by this technique are less ordered than mesoporous materials produced with ionic surfactants, when proved by XRD and SEM technique. They have, however, a mono-dispersed pore diameter, thicker pore walls, and a higher thermal stability.

The last approach, Santa Barbara researchers [10] has contributed largely to the development of the mesoporous materials, SBA-15. The SBA-15 was synthesized using amphiphilic triblockcopolymers, poly(ethylene oxide)–poly(propylene oxide) – poly(ethylene oxide), as a structure directing agent. This material has long range-order of hexagonal, large mono-dispersed mesopore (compared with zeolite, this material is characterized to compose of larger pore size up to approximately 30 nm and allows bulky molecules to enter into their pores) and thicker pore walls which make them more thermally and hydrothermally stable than previous materials. However this purely siliceous mesoporous material SBA-15 is lack of acid sites and

acidity, therefore incorporation of aluminum into SBA-15 structure, denoted as Al-SBA-15, was investigated in order to create acid sites. With the presence of acid sites, the activity of SBA-15 will be enhanced in the acid catalytic.

1.2.2 Catalytic cracking of plastic with heterogeneous catalyst

In 2001, Yanik *et al.* [11] studied the catalytic cracking of plastic waste, *i. e.* PVC, mixture of PVC/PE, mixture of PVC/PP over red mud, a by product from alumina manufacture process. Red mud showed good effect on adsorbing the emitted HCl from cracking but it had no effect on catalytic cracking of polymers as described in Table 1.2.

Table 1.2 Product yields obtained from cracking of PE and PP at 430°C

Plastic	Catalyst	Gas (wt %)	Liquid (wt %)	Residue (wt %)
PE	None	14.4	68.2	16.8
	Red mud	15	70.6	13.4
PP	None	12.7	72.6	14.7
	Red mud	15.4	72.2	12.4

Gobin *et al.* [12] have studied the cracking of polyethylene over various microporous materials – zeolites, clays and their pillared analogues. Because of the strong acidity of zeolitic materials, severe over cracking took place resulting into the formation of small molecules that were collected mainly in gaseous fraction, increasing its yield. Hence the yield to liquid fuel decreased.

In 1997, Aguado *et al.* [13] investigated the catalytic conversion of polyolefins into liquid fuels over MCM-41 compared with ZSM-5 and amorphous SiO_2-Al_2O_3. As compared to ZSM-5, MCM-41 exhibited a lower activity for cracking of HDPE and LDPE, which can be related to the higher acid strength of zeolite. In contrast, the cracking of polypropylene, high substituted plastic, showed the opposite result due to the steric hindrance of PP molecules was not allowed to enter into the narrow pores of zeolite. However, the product distribution of both PE and PP cracking showed that mesoporous material MCM-41 was more selective to the liquid range product than ZSM-5 and amorphous SiO_2-Al_2O_3.

Lin *et al.* [14] investigated the catalytic cracking of polypropylene using various catalysts including mesoporous material and the results were summarized in. Table 1.3. Because of larger pore size and weaker acidity as compared to zeolites, 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 selective to gaseous product which less valuable.

Table 1.3   Summary of PP cracking products over various catalysts at 360˚C

	Catalyst			
	HUSY	HZSM-5	HMOR	MCM-41
Yield (wt %)				
Gaseous	89.49	94.77	88.29	86.19
Liquid	3.75	2.31	4.54	5.07
Residue	6.76	3.92	7.17	8.74
Product distribution (wt %)				
C_1-C_4	36.73	67.41	59.86	25.47
Gasoline (C_5-C_9)	51.83	25.54	27.95	60.56
BTX	0.93	1.82	0.48	0.16

The effect of reaction temperature was also studied in their work. Product distributions from HUSY catalyzing pyrolysis of PP at different reaction temperatures were shown in Table 1.4. As a temperature of reaction was increased, yield of gaseous products increased but liquid yields decreased. It can be concluded that both yield and selectivity could be further influenced by the change in reaction temperature.

Table 1.4 Product distributions from HUSY catalyzing pyrolysis of PP at different reaction temperatures (fluidized bed reactor, N_2 flow rate 570 mlmin^{-1} and polymer/catalyst ratio = 40 wt %)

	Reaction temperature				
	290°C	330°C	360°C	390°C	430°C
Yield (wt %)					
Collection time(min)	30	20	15	15	15
Gaseous	85.52	87.61	89.49	91.78	93.71
Liquid	5.92	4.26	3.75	2.64	1.12
Residue	9.56	8.13	6.76	5.58	5.27
Product distribution (wt %)					
C_1-C_4	34.31	35.98	36.73	37.24	37.88
Gasoline (C_5-C_9)	51.08	51.22	51.83	53.56	54.71
BTX	0.13	0.41	0.93	0.98	1.12

Recently, Aguado *et al.* [3] reported that the catalytic activity of acid solid catalysts i.e. ZSM-5, zeolite Beta, Al-MAM-41 and Al-SBA-15 have been related to its capacity to shift the degradation reaction to the lower temperature. Table 1.5 contains a numerical data describing the temperature of maximum reaction rate in catalytic cracking over those catalysts and amorphous silica (SiO_2). The result showed no effect in the cracking temperature when SiO_2 was used, which confirmed the lack of catalytic activity of non-acid solid catalyst. Despite showing strong acid property, ZSM-5 exhibited a very low catalytic activity on LDPE. The temperature of maximum degradation rate (T_{max}) for LDPE/ZSM-5 was 443°C, only 33°C below the thermal cracking temperature which was attributed to the diffusion impediments that affected the access of bulky molecule of polymer to its internal active sites. T_{max} for LDPE cracking by Al-MCM-41, zeolite Beta, and Al-SBA-15 were remarkably reduced to 407, 417 and 417°C, respectively.

Table 1.5 Parameter describing the thermal and catalytic degradation of polyethylene samples [3]

Polymer	Catalyst	$T_{initial}$ (°C)	T_{max} (°C)
LDPE	No	419	476
	SiO_2	419	476
	ZSM-5	374	443
	Beta	370	417
	Al-MCM-41	367	407
	Al-SBA-15	372	417
HDPE	No	431	479
	SiO_2	431	479
	ZSM-5	385	418
	Beta	385	425
	Al-MCM-41	355	421
	Al-SBA-15	343	426

where, T_{max} : Temperature of the maximum reaction rate

The cracking of plastic mixtures, LDPE and ethylene vinyl acetate (EVA) copolymer over nanocrystalline H-ZSM-5, Al-MCM-41 as well as Al-SBA-15 has been conducted by Serrano *et al.* [15]. Although nanocrystalline ZSM-5 gave the highest conversion about 80% at 400 °C and more than 90% at 420 °C as shown in Figure 1.4 but the selectivity to the light oil fraction (C_6-C_{12}) in Figure 1.5 was only about 20% while those of Al-MCM-41 was approximately 45% and Al-SBA-15 gave the highest selectivity up to 55% of light oil fraction.
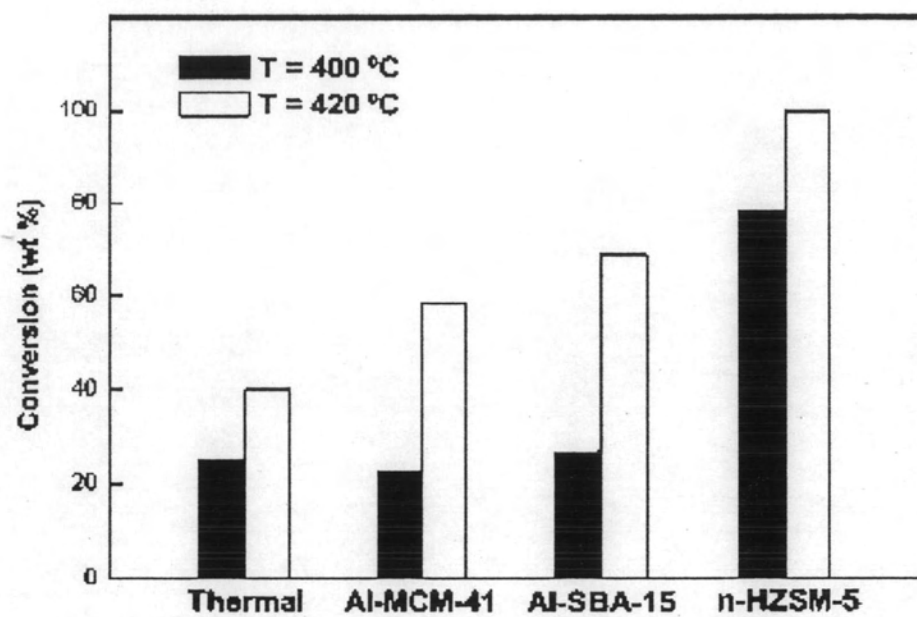
Figure 1.4 Conversions obtained in the thermal and catalytic cracking of the plastic mixture at different temperatures.
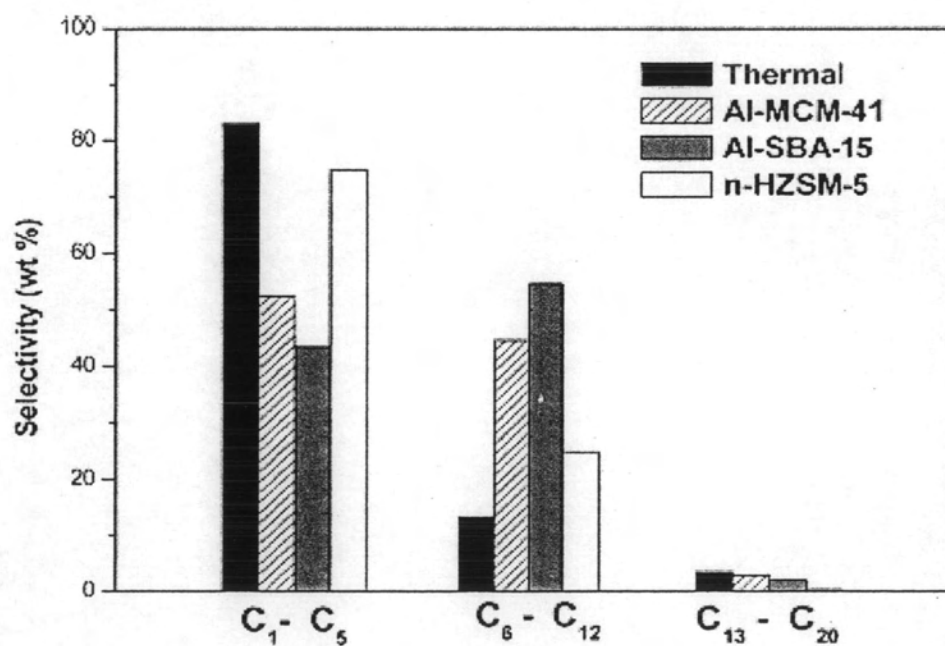

Figure 1.5 Selectivity by groups obtained in the thermal and catalytic cracking of the plastic mixture at 420°C.

1.2.3 The development of synthesizing Al-SBA-15

Since Santa Barbara researchers [10] has contributed largely to the development of the mesoporous materials, SBA-15 which synthesized using amphiphilic triblockcopolymers, poly(ethylene oxide) − poly(propylene oxide) − poly(ethylene oxide), as a structure directing agent. This material has long range-order of hexagonal, large mono-dispersed mesopore (compared with zeolite, this material is characterized by larger pore size up to approximately 30 nm and allows bulky molecules to enter into their pore) and thicker pore walls which make them more thermally and hydrothermally stable than previous materials. However this purely siliceous mesoporous material SBA-15 is lack of acid sites and acidity, therefore incorporation of aluminum AlSBA-15 was investigated in order to create acid sites. With the presence of acid sites, the activity of SBA-15 will be enhanced in the reaction involving acid catalyst.

Mesoporous silica SBA-15 can be incorporated with aluminum via two different synthesis procedures that are direct synthesis and post-synthesis procedure. The direct synthesis procedure often required a specialized synthesis conditions depending on the respective structures of the materials, and the incorporation of aluminum into the silica matrix usually caused a decrease in the structural ordering [16]. In 1999, Yue *et al.* have synthesized Al-SBA-15 by changing the synthesis condition from a strongly acidic condition (pH < 0) to a pH value of 1.5 [16]. However, such aluminum incorporation was not efficient because a large proportion of extra framework aluminum species was observed by ^{27}Al NMR as shown in Figure 1.6. The ^{27}Al-NMR spectra of Al-SBA-15 (Si/Al = 7) prepared with this method exhibited the presence of two aluminum signals at the chemical shifts of about 50 and 0 ppm. Typically, the former signal refers to the framework site and the latter signal ascribes to the non-framework site. More recently, a more effective direct synthesis method, so called "pH adjusting method" [17], has been reported. The pH adjusting method involves a two-step approach, in which the conventional low pH of the sol−gel reaction was adjusted up to neutral (pH 7.5) for further crystallization. Compared to other direct synthesis methods, the pH adjusting method could introduce more Al into mesoporous silicas. However, the synthesis procedures were relatively complicated.
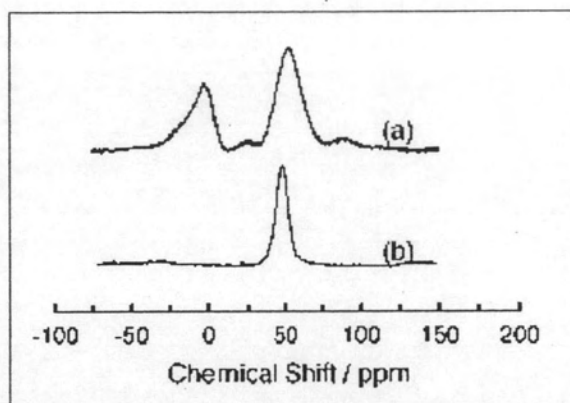
Figure 1.6 ^{27}Al-NMR spectra of AlSBA-15 prepared with direct synthesis procedure with the Si/Al ratios: (a) AlSBA-15(7) and (b) AlSBA-15(45).

Later, Li *et al.* made use of this method combined with a hydrolysis-controlled approach to prepare Al-SBA-15 with the Si/Al ratios in the range of 22–53. Recently, a novel method using preformed zeolitic nanocluster precursors for the incorporation of heteroatoms into the mesoporous silica synthesized in strongly acidic media has been reported by Han and co-workers [18] and Liu and Pinnavaia. The aluminum atom was first incorporated into the framework of the preformed zeolitic nanoclusters and then directly introduced into the mesostructure through the assembly with the surfactant. Although the materials obtained from that method showed high catalytic activity, the aluminum content in these materials was still relatively low. When the Si/Al ratio in the initial gel for mesoporous aluminosilicates-9 (MAS-9) was 40, for example, the Si/Al ratio was only 89 in the final product. As described above, the direct synthesis of Al-SBA-15 is difficult and often not stoichiometric.

From this viewpoint, therefore, the development of a simple post-synthesis method for the alumination of the mesoporous silicas that are synthesized under strongly acidic conditions becomes an appealing alternate choice. In comparison to MCM-41 and MCM-48, however, relatively few post-synthesis alumination methods for SBA-15 have been reported in the literature.
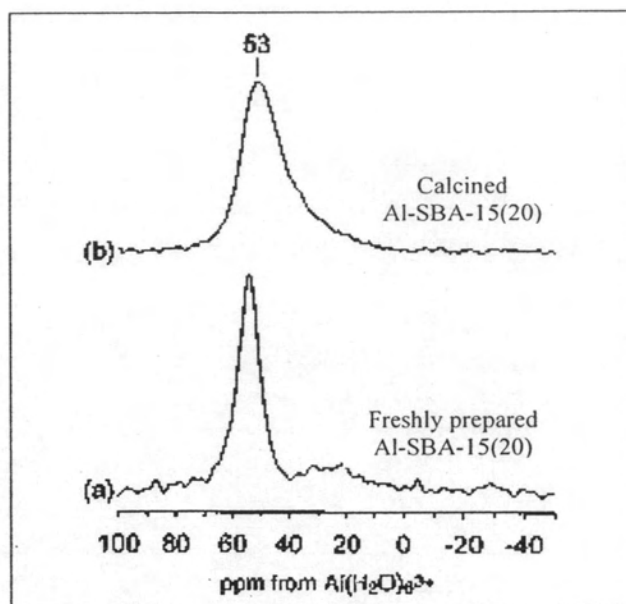
Figure 1.7 ^{27}Al-MAS-NMR spectra of AlSBA-15 prepared by post-synthesis of SBA-15 with sodium aluminate in aqueous solution: (a) before and (b) after calcination.

As shown in Figure 1.7 the Al-SBA-15 samples prepared with post-synthesis procedure developed by Luan and colleagues [19] exhibited only a signal at 53 ppm, tetrahedral aluminum form. Furthermore, the materials produced via these post-synthesis procedures have superior structural integrity, acidity and catalytic activity to those of materials having aluminum incorporated during synthesis [17, 19].

Kao *et al.* have developed the post-synthesis alumination method for SBA-15 using an aqueous $(NH_4)_3AlF_6$ solution as the aluminum source [20]. This alumination method was first reported by Chang *et al.* for the incorporation of Al^{3+} into the high silica ZSM-5 framework [21]. The Al-SBA-15 material thus obtained exhibits a high framework aluminum content (up to a bulk Si/Al molar ratio near 5), good structural integrity, and well-developed Brønsted acidity.

From these literature reviews, mesoporous material Al–SBA-15 showed remarkable performance relative to conventional catalyst. Despite the catalytic activity, the importance in this reaction involved the stability of catalyst. The development of high stability heterogeneous catalyst for catalytic cracking of waste plastic has been an important goal for industrial nowadays.

1.3 Objectives

1. To synthesize and characterize mesoporous material SBA-15 and develop the post synthesis of Al-SBA-15 with various Si/Al molar ratios.
2. To study the effect of reaction temperature, polymer to catalyst ratio, and Si/Al ratio of catalyst in catalytic cracking of polypropylene over Al-SBA-15.
3. To apply the optimum conditions for cracking of waste polypropylene.

1.4 Scope of work

Synthesis of SBA-15 [10], and Al-SBA-15 [19] by hydrothermal method was investigated using triblock copolymer as pore directing agent. The Si/Al molar ratios in gel or reactant mixture were varied from 10 to 100. The optimum condition for cracking of polypropylene over Al-SBA-15 was determined by studying the effects of treatment routes for ion exchange, temperatures, catalyst amounts, and Si/Al ratios. They were tested for their activity in the catalytic cracking of polypropylene waste under optimum condition.