

EFFECTS OF ZEOLITE ON THE CATALYTIC DEGRADATION OF POLYPROPYLENE

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Abstract: Effects of zeolite on the catalytic degradation of polypropylene (PP) at atmospheric pressure were studied by a batch operation. The degradation of PP was carried out between temperature 325 °C and 500 °C. HY, silica-alumina, and H-ZSM5 were shown degradation activity. The percentage of PP degradation with active catalysts was more than 97% in comparison with that of 6.96% for thermal degradation at 400 °C. The product proportion included liquid, gaseous, and solid residue for thermal and catalytic degradation were different. The percentage degradation of PP was almost independent of the kinds of PP in thermal degradation. In catalytic degradation, the powder and film of PP samples with HY had higher percentage degradation than pellet PP when the temperature was lower than 375 °C. HY had shown the most active between temperatures 325 °C and 375 °C. Pyrolyzer GC/MS was used to analyze the gaseous product distribution and showed not only the number of gaseous product was reduced but also the products shifted to lower carbon number when PP was degraded over HY and the results were different from the thermal and catalytic degradation of PP with silica-alumina and H-ZSM5.

Keywords: polypropylene; degradation; catalyst; zeolite; plastic recycling

1. Introduction

Polypropylene is a very useful industrial plastic raw material to manufacture many kinds of useful products such as containers, fibers, battery cases, car bumpers, dashboards, film and sheet, and so on. According to the report [1], in the year of 2009, the global PP consumption will reach 51.3 million m.t. and the global demand of PP will grow by 6.96% a year until 2010. Over the past five years from 2007, PP production has risen by 34% and PP consumption by 35%, the production capacities will grow at an average of 5.9%. Such a large amount of PP was used to manufacture variety of daily necessities and the PP wastes become one of the main components in the solid waste stream. The recycling of post-consumer PP products, just like the other plastics products, become more and more important because of both environmental protection and economic benefits.

Degradation (or pyrolysis) is a chemical method for recycling plastic wastes in the absence of oxygen [2]. Degradation of plastics over an active catalyst has many advantages and it is a resourceful treatment route [3]. The effects of catalyst on the PP degradation have been studied by many authors. Zeolite was the most frequently utilized as a catalyst in such a process. The zeolites had been tested as catalyst in PP degradation including ZSM-5 [4-9], silica-alumina [9-11], Y, L and mordenite [5], as well as silica gel and mesoporous silica [8, 11]. The effects of each kind of catalyst on the PP degradation were different due to their frame structures, properties, and reaction conditions.

In this work, thermal and catalytic degradation of PP with zeolite catalysts have been studied. Product proportions, effect of kinds of PP, reaction temperature, and time in catalytic process were compared with those of thermal degradation. The effect of active catalysts on the gaseous product distributions was also investigated by pyrolysis GC/MS analyses.

2. Experimental

PP pellet (BOPP grade, 3.0 mm in size and sphere in shape) was obtained from Formosa Plastics Co., Taiwan. PP powder (0.5 ~ 1.0 mm in size) was prepared by grinding PP pellet and PP film (3 x 3 mm in size and square in shape) was cut from a sheet of shrink film which was made from PP pellet. The zeolite catalysts include HY, silica-alumina, hydrogen form of ZSM5, hydrogen form of mordenite, sodium form of mordenite, 13X, and 4A.

The apparatus and degradation procedures of PP were described in detail in previous reports [12]. The product proportion was calculated as the ratio of the product weight to the initial PP weight and multiplied by 100%. The percentage degradation of PP (α) is calculated by the percentage of PP weight loss over the initial weight of PP. The analysis of gaseous product distribution was performed using a pyrolyzer GC/MS with a HP-5MS capillary column (ϕ 0.25 mm x 30m).

3. Results and discussion

3.1 Effect of zeolite

Tab. 1 shows the effect of zeolites on the percentage of PP degradation (α). In thermal degradation, α value of the pellet PP was only 6.96% at 400 °C. Values of α were very different from PP catalytic degradation. HY, silica-alumina, and H-ZSM5 were found the most active in PP degradation. The pellet PP almost decomposed completely at 400 °C with these active catalysts. The activity of H-mordenite on PP degradation was moderate, however, Na-mordenite was almost none. Zeolite with stronger acidity enhanced the degradation ability of plastics as described by Sakata et al. [9]. The proportion of liquid, gaseous product and solid residue of pellet PP thermal and catalytic degradations are listed in Tab. 2. In thermal degradation, the proportion of liquid and gaseous product was minor and the solid residue was major. The proportion of solid residues was 90.7%. The solid residue became minor when PP

PART I PYROLYSIS

was degraded with active catalysts, especially with HY (reduced from 90.7% to 0.41%). The majority was gaseous product for PP catalytic degradation over active catalysts and the proportion could reach as high as 99.45% for HY and the lowest for silica-alumina (65.0%). The proportion of liquid product, on the contrary, was the highest for silica-alumina (32.6%) and the lowest for HY (0.14%).

Tab. 1 Effect of zeolite on pellet PP thermal and catalytic degradation ^{a)}

Zeolite	α (%)	
	Zeolite	PP + Zeolite
-	—	6.96 ^{b)}
Si-Al	14.9	97.5
HY	15.4	99.6
H-ZSM5	5.4	97.8
H-mordenite	9.2	59.8
Na-mordenite	10.0	6.5
13X	13.1	8.1
4A	13.7	6.9

^{a)} reaction temperature: 400 °C, reaction time: 1 h, nitrogen flow rate: 100 mL/min,
weight ratio of PP/catalyst = 10/1

Tab. 2 Product proportions for pellet PP thermal and catalytic degradation ^{a)}

	Weight (%)		
	Gas	Liquid	Residue
thermal	6.1	0.9	93.0
HY	99.45	0.14	0.41
H-ZSM5	82.4	15.4	2.2
Si-Al	65.0	32.6	2.4

^{a)} reaction temperature: 400 °C, reaction time: 1 h, nitrogen flow rate: 100 mL/min

3.2 Effect of temperature

The dependence of α value for thermal and catalytic degradation of PP with HY on the degradation temperature is shown in Tab. 3. The percentage of PP degradation was increased dramatically from about 7% to 90% in the temperature range of 400 °C and 450 °C. When the temperature was raised to 500 °C, PP samples could be decomposed nearly 100%. In the catalytic degradation, the α value of PP with HY is much higher than that of in thermal degradation. There are two different phenomena to be noticed between thermal and catalytic process. First, the degradation onset temperature in catalytic process is much lower than in thermal process, especially for PP powder and film (much lower than pellet). Second, the powder and film PP has better degradation ability than pellet PP when temperatures are lower than 375 °C in catalytic degradation. When temperature was increased to 400 °C, all kinds of

PP samples with HY could be completely decomposed. The results suggested the degradation ability of PP depends on the uniformity and extent of contact between PP and catalyst if temperature is not high enough. The mixing is more uniform and/or the contact surface is more sufficient resulted in higher percentage degradation of plastics. Fig. 1 illustrated the effect of temperature on the percentage degradation of pellet PP with and without HY, H-ZSM5, and silica-alumina. The figure showed the degradation of PP was higher in catalytic process than in thermal process when the temperature was higher than 325 °C. It also demonstrated the degradation temperature could be lowered down about 75 °C to obtain the same percentage degradation when active catalysts were added to the PP samples. In case of pellet PP catalytic degradation over active catalysts, the α values of PP approximately kept constant when degradation temperatures were lower than 325 °C or higher than 375 °C. Nevertheless, PP with HY exhibited better degradation activity than H-ZSM5 and silica-alumina between these two temperatures.

Tab. 3 Effect of temperature on pellet PP thermal and catalytic degradation with HY catalyst

Temp (°C)	α (%)		
	Pellet	Powder	Film
thermal ^{a)}			
350	0.02	1.17	0.20
400	6.96	7.01	7.13
450	91.8	94.1	89.4
500	99.4	99.2	99.1
PP+HY ^{b)}			
325	5.3	30.0	31.8
350	22.2	46.4	46.2
375	58.6	76.1	75.5
400	99.6	99.3	99.7

a) time: 1 h, nitrogen flow rate:100 mL/min;

b) time: 1 h, nitrogen flow rate:100 mL/min, weight ratio of HY/PP = 10/1

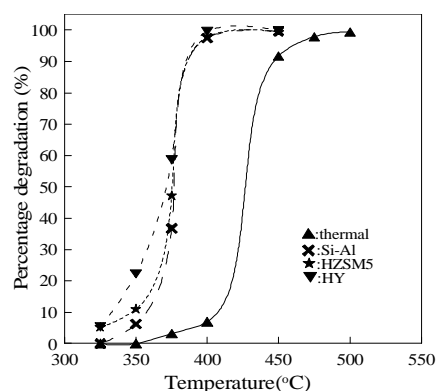


Fig. 1 Effect of temperature on pellet PP degradation for 1 h

3.3 Effect of degradation time

Fig. 2 shows the percentage of pellet PP degradation in thermal and catalytic degradation at 400 °C as a function of degradation time. A similar trend was found for the catalytic degradation of pellet PP with HY, H-ZSM5, and silica-alumina. The degradation of PP increased as the time increased and completely decomposed at time of 60 min. With HY, not only the percentage of PP degradation was higher than with the other two zeolites but also took a shorter time to reach the maximum decomposition. The percentage of PP degradation in thermal degradation was extremely small in comparison with the catalytic degradation.

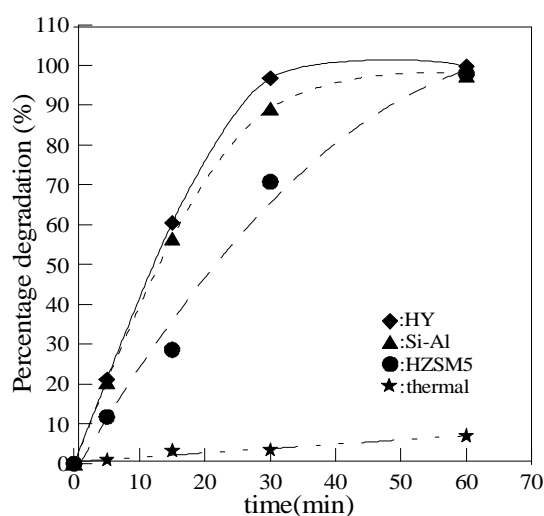


Fig. 2 Effect of time on PP degradation at 400 °C

3.4 Analysis of gaseous products

The gaseous product distributions were analyzed by pyrolyzer GC/MS at 445 °C for 6 seconds and the results were demonstrated in Fig. 3. In thermal degradation, the products were in a broad distribution between 3 and 24 carbons. The main products were ranging from C9 to C16 and the most abundant one was C14 with 16 wt%. In the catalytic degradation, the product distribution of PP with H-ZSM5 and with silica-alumina catalysts was also distributed in a wide carbon number range and both were similar with the results of thermal degradation. The main products for these two catalytic reactions were ranging from C14 to C16 and both were centered at C14 with the highest percentage (24% and 28%), respectively. In the case of PP with HY, the result was very different from with thermal degradation and PP with the other two zeolites. The gaseous products obviously not only shifted to the compounds with lower carbon numbers but also narrowed down to the range of C4 to C12 and the main products were between with 6 carbons and 10 carbons. The most abundant product was C8 compounds and with the amount of 26 wt%. HY clearly has the ability to change the gaseous product distribution and produces the hydrocarbon products with a lighter fraction. The catalytic effect of zeolite HY on the degradation of PP was different from with the other two kinds of zeolites.

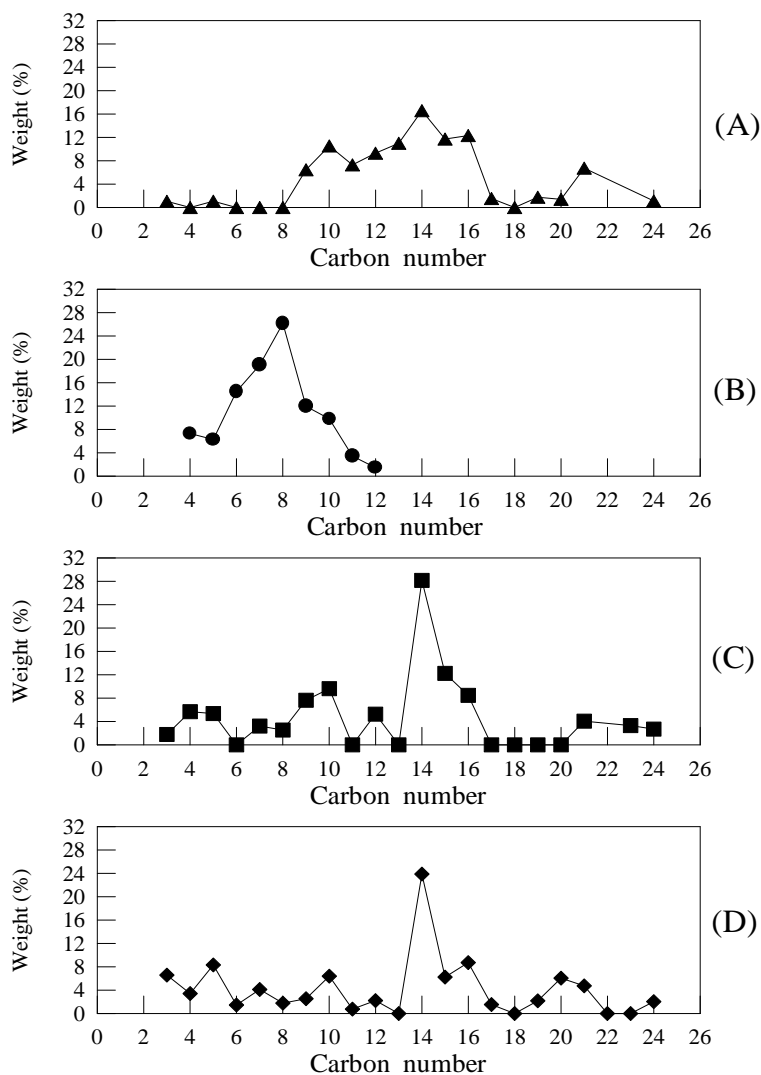


Fig. 3 Carbon number distribution of pyrolyzed gaseous products of pellet PP at 445°C for 6 sec; (A) thermal, (B) PP+HY, (C) PP+Si-Al, (D) PP+H-ZSM

4. Conclusions

HY, H-ZSM5, and silica-alumina are effective zeolites in the catalytic degradation of PP. It can substantially enhance the degradation ability of PP and change the product proportion. HY is the most active catalyst. Degradation temperature is the most important factor on the degradation of PP. In catalytic degradation, type of zeolite and contact between PP and zeolite are the other important factors. HY is the zeolite not only could significantly change the gaseous product distributions but also shift the produced hydrocarbons to a lighter fraction.

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PART I PYROLYSIS

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