

Pyrolysis of an LDPE-LLDPE-EVA copolymer mixture over various mesoporous catalysts

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Abstract—The aim of the present work was to study the performance of mesoporous catalysts in the catalytic cracking of an LDPE+LLDPE+EVA copolymer. Mesoporous catalysts, including MCM-41, Nano-MCM-41, Al-Nano-MCM-41, MMZ-ZSM-5 and Meso-MFI, were applied for this reaction. Also, microporous HZSM-5 was used for a comparison. All of the catalysts showed higher decomposition abilities than thermal decomposition. The catalytic conversion of the LDPE+LLDPE+EVA copolymer was highest with the use of Meso-MFI due to its pore size and strong Brönsted acidity, with high selectivity for lower olefin and gasoline range hydrocarbon. Both MMZ-ZSM-5 and Al-Nano-MCM-41 have an acid site that induced the decomposition reactions, and thus, produced compounds with lower carbon numbers in liquid products. MCM-41, which exhibits no acidity, showed a similar distribution of liquid products to that via thermal cracking, while Nano-MCM-41 showed better catalytic cracking ability due to its high surface area.

Key words: Catalytic Pyrolysis, LDPE+LLDPE+EVA Copolymer Mixture, Mesoporous Catalysts, Acidity

INTRODUCTION

In Korea, waste plastics have generally been landfilled or incinerated, which has posed serious environmental problems. The pyrolysis of waste plastics has drawn attention because it has been recognized as being more environmentally sound than conventional treatment methods. Furthermore, pyrolysis can convert waste plastics into valuable gas, oil and solid products [1]. Accordingly, the pyrolysis of waste plastics is an emerging technology for resolving the problem of troublesome wastes.

In particular, waste agricultural film has been noted as an environmental problem among waste plastics in farming villages. The output of agriculture film in Korea is about 100,000 tons/year, and most farming villages are overrun by waste film [2]. The lifetime of these films is only about 1-2 years, as they undergo degradation due to solar radiation and oxidation, etc. It is necessary to develop a method for the treatment of waste agricultural film without the production of environmental pollution. Much interest has concentrated on pyrolysis studies, as an environment-friendly technology, for the treatment of waste agriculture film. Pyrolysis, however, has suffered from several disadvantages, such as low selectivity and high energy input [1-5]. Catalytic pyrolysis was introduced to improve the product selectivity and reduce the energy input.

The required properties of highly active catalysts for the pyrolysis of plastics are a large external surface area, bent and large pores for suppressing carbon deposits and rapid mass transfer of reactants and products. Many investigations have used various zeolites:

ZSM-5, Y, beta, mordenite, ferrierite and SAPO, etc. [6-14], of which ZSM-5 has been intensively investigated due to its acidity. The application of ZSM-5 to the pyrolysis of waste plastics, however, has encountered technical problems, such as relatively high quantity of gas products and coke formation close to the pore entrances. Mesoporous materials would be alternatives to minimize the problems caused in the application of ZSM-5. MCM-41 has high potential as a catalyst for the pyrolysis of waste plastics due to its high surface area, tunable uniform mesopores (from 20 to 100 Å) and weak acidic strength. MCM-41, however, has only mild acidity and poor hydrothermal stability, thus inhibiting their use in high-temperature processes in the presence of steam.

An interesting approach to mesoporous catalysts is the preparation of mesoporous materials constructed with zeolitic frameworks, which may give synergistic advantages from zeolites and mesoporous materials. For example, the hydrothermal stability and acidity of the mesoporous materials are relatively low compared with those of zeolites, which strongly influences their practical applications in industry. Several works have reported on the preparation of zeolitic mesoporous materials [15-21]; however, their application to the catalytic cracking of an LDPE-LLDPE-EVA copolymer mixture, with a composition similar to that found in real agricultural film wastes, has never been reported.

The aim of the present work is to compare the performance of mesoporous materials in the catalytic cracking of an LDPE-LLDPE-EVA copolymer mixture. Various mesoporous materials, such as MCM-41, Nano-MCM-41, Al-Nano-MCM-41, MMZ-ZSM-5 and Meso-MFI, were applied as reusable heterogeneous catalysts for the pyrolysis of a polymer mixture. Catalytic cracking over microporous HZSM-5 was also conducted for a comparison.

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EXPERIMENTAL

1. Materials

The polymer mixture used in this work contained LDPE (BF500, $M_n=20,000$, $M_w=144,000$, Melt Index=3.0 g/10 min, density=0.92 g/cm³), LLDPE (UF315, $M_n=32,000$, $M_w=175,000$, Melt Index=1.0 g/10 min, density=0.923 g/cm³) and EVA copolymer (VS430, (-CH₂-CH(O₂CCH₃))_x(-CH₂-CH₂-)_y, 19.0 wt% vinyl acetate, $M_n=18,000$, $M_w=115,000$, Melt Index=2.5 g/10 min, density=0.939 g/cm³), which were provided by Hyundai Petrochemical Co., Ltd.

2. Catalysts

The mesoporous silica, MCM-41, was synthesized following the procedures described elsewhere [22-24], but in brief: cetyltrimethylammonium bromide (CTAB) (12.15 g) was completely dissolved in 140 g of distilled water for a few minutes using an oven (100 °C), after which, 50 g of a sodium silicate solution (Na/Si=0.5) was added dropwise at room temperature. After stirring for 1 h to form a gel, the mixture was aged at 100 °C for 24 h. Acetic acid (50 wt%) was added until the mixture pH was 10. In addition, the mixture was aged at 100 °C for 24 h. A pH of 10 was re-established using the previous method. The final solid products were obtained by filtration and then washed several times with distilled water. The solid product was calcined at 550 °C for 4 h.

The syntheses of mesoporous materials from ZSM-5 (MMZ-ZSM-5) were performed as follows: First, the NaOH solution was prepared in typical conditions by dissolving 1.5 g of NaOH in 5.0 g of deionized water. Subsequently, 2.25 g of HZSM-5 was added into the NaOH solution under magnetic stirring, to give a clear solution. Finally, the dissolved zeolite solution was diluted using 2.5 g of deionized water and used as the framework source for the MMZ materials. 4.6 g of CTAB was dissolved in 70 g of water. The above zeolite solution was added dropwise into the CTAB solution. The reaction mixture was then heated at 100 °C for 24 h. The white precipitate formed was filtered, washed with water and dried overnight at 100 °C. The MMZ material thus obtained was washed with an HCl/ethanol mixture and finally calcined at 550 °C for 3 hrs to remove the surfactant.

The mesoporous MFI zeolite (Meso-MFI) was synthesized following the procedures described elsewhere [18,19].

In a typical synthesis of nanosized MCM-41 (Nano-MCM-41), 6.13 g of tetraethylorthosilicate was added to a hydrochloric acid solution (52.5 g pH 0.5), containing 18.24 g of cetyltrimethylammonium chloride, 3.5 g of a triblock copolymer and 2.2 g of a poly(ethylene glycol) mono-octyl-phenyl ether, at 10 °C. The reaction mixture became a clear solution with stirring. After being stirred for 24 h, the solution changed into a white emulsion-like solution on the addition of 7.5 g of aqueous ammonia solution (14.7 M), and was then stirred at 10 °C for 24 h. The white product was recovered by filtration, washed with distilled water, and dried overnight at 80 °C. The organic moieties in the sample were removed from the dried products by calcination in air at 550 °C for 3 h.

The incorporation of aluminum into Nano-MCM-41 was performed using the post-synthetic grafting method. Before baking, the prepared Nano-MCM-41 was introduced into a solution prepared by dissolving AlCl₃ in 100 mL of ethanol, according to the required Si/Al ratio, stirred for 24 h, washed with ethanol, filtered, dried for 24 h, and then calcined at 550 °C for 4 h.

3. Catalyst Characterization

Nitrogen adsorption-desorption isotherms at 77 K were obtained using a Micromeritics ASAP 2010 apparatus. Previously, all samples were subjected to a standard outgassing procedure at 200 °C, under vacuum, for 5 h. The surface areas were obtained via the BET procedure.

Ammonia temperature programmed desorption (TPD) measurements of the catalysts were performed in a Micromeritics 2900 TPD apparatus. The samples were out-gassed under an He flow (50 ml/min), with a heating rate of 15 °C/min, from room temperature to 550 °C. This final temperature was maintained for 1 h, with the samples subsequently cooled to 180 °C and treated with an ammonia flow (30 ml/min) for 30 min. The physisorbed ammonia was removed from the sample by flowing He at 180 °C for 2 h. The chemically bound ammonia was determined by increasing the temperature to 550 °C, with a heating rate of 15 °C/min. The ammonia present in the effluent stream was continuously monitored with a thermal conductivity detector (TCD).

4. Catalytic Pyrolysis

Thermal and catalytic cracking studies were performed in a Pyrex semi batch reactor, at atmospheric pressure, under a nitrogen flow (Fig. 1). Weights of 0.05 and 10 g of the catalyst and polymer were loaded into the reactor and thoroughly mixed. Thereafter, the reactor was equipped with an external electronic heating furnace, and heated at a rate of 20 °C/min to the reaction temperature (410 °C), which was maintained for 2 h and continually monitored by using a thermocouple in direct contact with the reaction mixture. In our previous study using TGA, the polymer mixture with catalyst decomposed rapidly about 410-420 °C; therefore, catalytic performance was tested at 410 °C [2]. The gaseous products obtained at this reaction temperature were swept out from the reactor by a nitrogen stream, and separated into liquid and gaseous fractions via a condenser cooled using a chiller. The liquid fraction was collected from the bottom of the condenser and weighed. The effluent gas flow was continu-

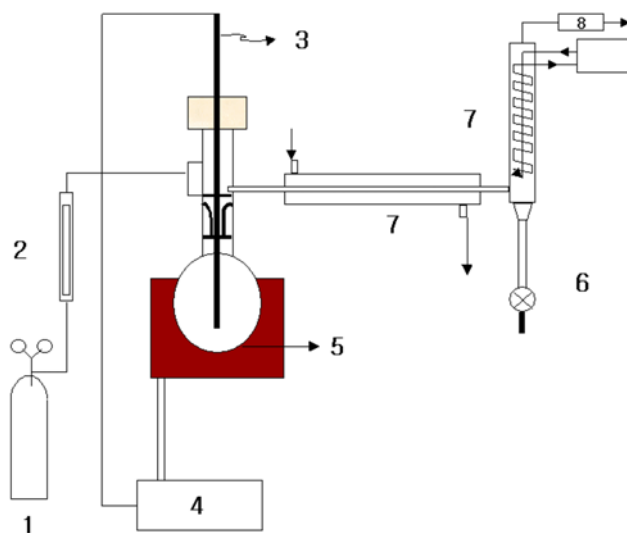


Fig. 1. Experimental apparatus for catalytic pyrolysis.

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|----------------------------|-----------------------------|
| 1. N ₂ cylinder | 5. Flask |
| 2. Flow meter | 6. Liquid product collector |
| 3. Thermocouple | 7. Condenser |
| 4. Temperature controller | 8. Gas meter |

ously measured using a soap meter placed after the condenser, and was finally collected in a gas bag. The polymer conversion was defined as the sum of the collected gaseous and liquid products with respect to the initially amount of loaded polymer mixture.

The gaseous products were analyzed by a Younglin-M600D gas chromatograph, using a capillary column, HP-plot $\text{Al}_2\text{O}_3/\text{KCl}$, $50\text{ m} \times 0.322\text{ mm} \times 8.00\text{ }\mu\text{m}$, connected to an FID. The liquid products from the pyrolysis of the polymer were analyzed by gas chromatography (Shimadzu GC-2014), with a flame ionization detector and GC-MS (HP 5973), employing an HP-5M capillary column (0.25 mm i.d. and 30 m length).

RESULTS AND DISCUSSION

1. Catalyst Characterization

Table 1 shows the physical properties of the catalysts. The surface area of Nano-MCM-41 was higher than that of MCM-41. In addition, the BET surface areas and pore volumes of the Meso-MFI were much higher than those of the conventional HZSM-5 zeolite. This was attributed to the formation of mesopores, as described previously [18]. In addition, the pore size of the Meso-MFI was the largest of all the catalysts, suggesting that its porosity can allow large LDPE-LLDPE-EVA copolymer molecules or pyrolytic vapors de-

rived from the decomposition of LDPE-LLDPE-EVA copolymer to diffuse to the inside of the pores.

The NH_3 -TPD curves showed the acidic properties of the catalysts used in this study (Fig. 3). The HZSM-5 and Meso-MFI catalysts showed two major peaks. The peaks at approximately 180 and 380 °C were attributed to NH_3 desorption from the weak acid sites and strong Brönsted acid sites, respectively. The Meso-MFI showed a distribution of acidic sites analogous to that of conventional HZSM-5. Meanwhile, MMZ-ZSM-5 and Al-nano-MCM-41 exhibited smaller peaks at around 150 °C, suggesting the amount and strength of the acidic sites in MMZ-ZSM-5 and Al-nano-MCM-41 were much lower than those of the Meso-MFI and HZSM-5, particularly the strong acidic sites. In addition, MCM-41 and nano-MCM-41, which did not contain Al species, showed the lowest acidities.

2. Catalytic Activity

Table 2 shows the results with respect to the different catalysts

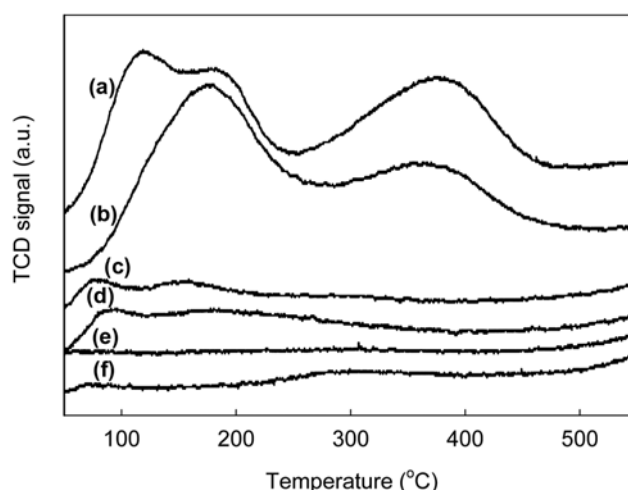


Fig. 2. NH_3 TPD of catalysts ((a) HZSM-5, (b) Meso-MFI, (c) MMZ-ZSM-5, (d) Al-Nano-MCM-41, (e) Nano-MCM-41, (f) MCM-41).

Table 1. Textural properties of catalysts

Catalysts	BET surface area (m^2/g)	Pore size (nm)
HZSM-5	389	0.51×0.55 [100] ^a 0.53×0.56 [010] ^a
MMZ-ZSM-5	456	2.7
Meso-MFI	633	4.7
Al-Nano-MCM-41	1084	2.5
Nano-MCM-41	1074	2.5
MCM-41	1041	2.9

^aChannel diameter viewed along [hkl] direction

Table 2. Product distributions of plastic mixture degradation

Products	Thermal	Catalysts					
		HZSM-5	MCM-41	MMZ-ZSM-5	Meso-MFI	Nano-MCM41	Al-Nano-MCM-41
Conv. (%) ^a	39.8	83.3	56.9	47.1	99.8	49.9	76.2
Yield (wt%)							
Gas	5.6	28.5	7.0	6.3	34.5	7.2	5.2
Liquid	34.5	54.8	49.9	40.8	65.3	42.8	71.0
Gaseous product distribution							
C ₁	12.2	0.2	4.8	3.1	0.3	8.2	4.1
C ₂	27.7	2.5	18.9	14.2	2.5	21.8	14.5
C ₃	22.4	30.7	35.7	28.5	37.1	32.1	32.0
C ₄	37.7	66.6	40.6	54.2	60.1	37.9	49.4
(i-C ₄ +i-C ₄) in C ₄	36.5	58.8	13.6	14.1	59.2	20.6	33.6
Olefin fraction in C ₂ -C ₄	73.1	77.8	49.7	60.9	87.8	61.2	59.2

Plastic mixture: LDPE 2.5 g, LLDPE 2.5 g, EVA copolymer 5 g

Catalyst/Polymer: 1/200

Reaction temperature: 410 °C

^aConversion: $\{(\text{Polymer}_{\text{initial}}) - (\text{Polymer}_{\text{final}})\} / \text{Polymer}_{\text{initial}}$ after 2 h reaction

and also indicates that the use of a catalyst could considerably improve the conversion rates compared to non-catalytic reactions. Especially, the micropore HZSM-5, as well as the micro- and mesoporous hybrid-pore Meso-MFI resulted in significant conversions of the plastic mixture and high amounts of gas-phase products. Mean-

while, the other mesoporous catalysts, including MCM-41, MMZ-ZSM-5, Nano-MCM-41 and Al-Nano-MCM-41, gave high liquid-phase yields. As seen in the ammonia TPD of Fig. 2, the strong acid sites of the HZSM-5 and Meso-MFI could easily decompose the plastic mixture, resulting in higher amounts of gas-phase products. In addition, the highest activity obtained with Meso-MFI may be ascribed to its pore size. The pore size of Meso-MFI was sufficiently large to allow decomposition of the polymer mixture and very easily allow the diffusion of the polymer mixture to the inside of the pores. Therefore, the high acidity and pore size resulted in Meso-MFI having the highest decomposition activity. With the use of ZSM-5 and Meso-MFI, high selectivities for olefin and i -C₄ were recorded, presumably due to the Brönsted acid sites.

On the contrary, the MCM-41 and nano-MCM-41 contained no acid sites, and thus did not show very high levels of activity. However, these two catalysts were more active than the non-catalytic reactions, due to their terminal Si-OH groups, which worked like a Brönsted acid site [25]. Sedeggi et al. [25] performed the catalytic cracking of high density polyethylene over silica MCM-41 catalysts. They proposed that the formation and stabilization of carbenium ions in the pores of the catalyst were due to the adsorption interaction between the polyethylenic fragments with the surface of the channels. The surface acidity of the all-silica MCM-41 was attributed to the presence of silanol groups.

Al-Nano-MCM-41 causes rapid increases in the reactions, due to the acidic sites created as a result of the incorporation of Al. However, most of the acidic sites were weak, which suppressed the production of gas-phase products and promoted the formation of liquid-phase products. Meanwhile, MMZ-ZSM-5 showed the lowest catalytic conversion of the plastic mixture irrespective of the presence of weak acidity. This might be ascribed to its having the lowest surface area. Fig. 3 presents the distribution of the liquid-phase products. The product distribution of MCM-41 with no acidic sites was similar with that of the non-catalytic reaction. The nano-MCM-41 produced compounds with relatively lower carbon numbers, as the increased surface area due to the nanosize multiplication caused more active decomposition reactions than MCM-41. Both MMZ-ZSM-5 and Al-nano-MCM-41 had acidic sites that induced decomposition reactions, and thus produced compounds with lower carbon numbers. Although the catalytic conversion with the use of MMZ-ZSM-5 was not good, the decomposition reaction for liquid-phase products was higher than that of MCM-41. The strong acidic Meso-MFI and HZSM-5 showed higher cracking abilities for liquid product producing compounds with lower carbon numbers. In general, the weak acidic or high surface area mesoporous catalysts produced diesel range hydrocarbons (around C₁₀ hydrocarbons), whereas the strong acidic catalysts produce gasoline range hydrocarbons (around C₅ hydrocarbons).

CONCLUSIONS

For the catalytic reaction of an LDPE+LLDPE+EVA copolymer, mesoporous catalysts, including MCM-41, Nano-MCM-41, Al-Nano-MCM-41, MMZ-ZSM-5 and Meso-MFI, showed higher cracking abilities than the non catalytic reaction. Especially, Meso-MFI, having the largest pore size and strongest Brönsted acidity, showed the highest cracking ability and selectivity for lower olefin and gaso-

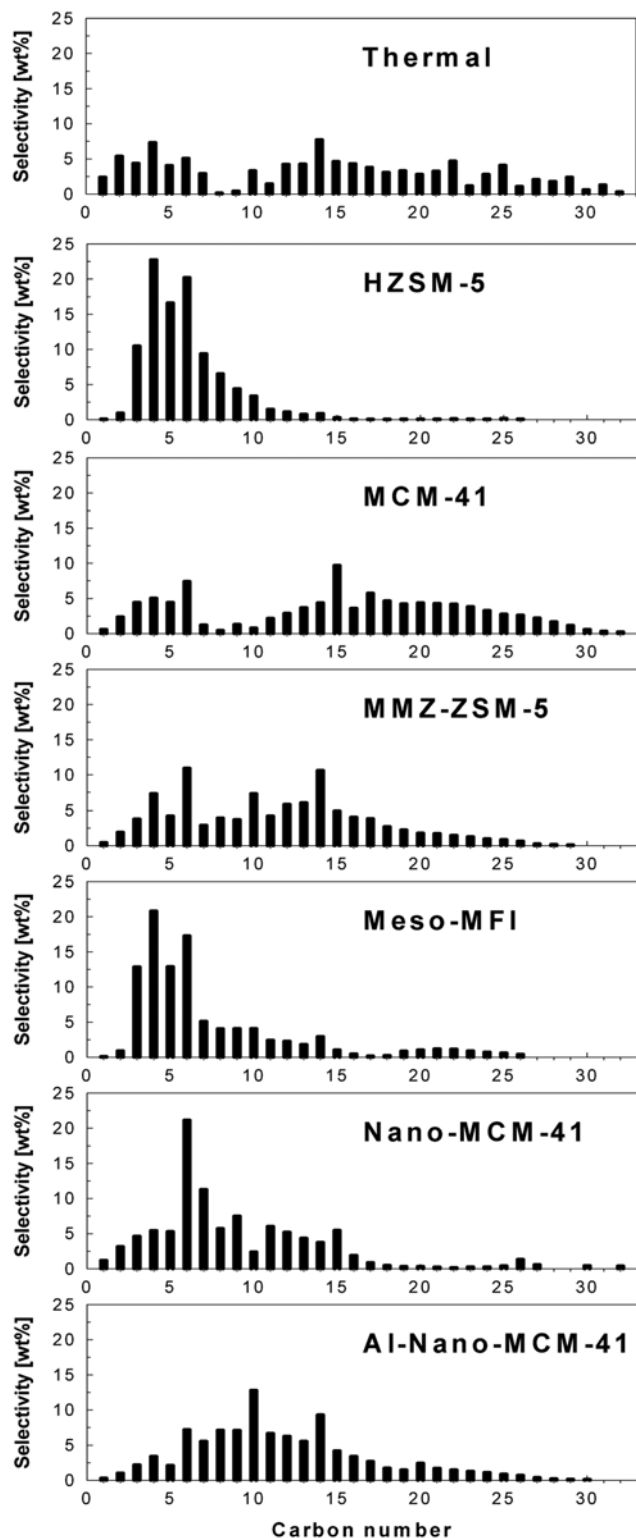


Fig. 3. Product distributions over various catalysts (Catalyst/polymer=1/200, Reaction temperature: 410 °C).

line range hydrocarbons. Microporous HZSM-5 showed similar activity to that of Meso-MFI. Meanwhile, other mesoporous catalysts, i.e., Al-Nano-MCM-41 and MMZ-ZSM-5, possessing weak acidities and high surface areas, produced diesel range hydrocarbons liquid products. MCM-41, which had no acidity, showed a similar liquid product distribution to that of thermal cracking, while Nano-MCM-41 showed better catalytic cracking ability due to its high surface area.

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