

Catalytic degradation of polyethylene over SBA-16

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(Received 10 April 2010 • accepted 14 May 2010)

Abstract—The performance of SBA-16 catalysts toward the degradation of two kinds of polyethylenes, high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), was evaluated by using a thermogravimetric analyzer and batch reactor. The effect of the acidity of SBA-16 upon degradation efficiency was investigated. Quantitative analyses of the products were conducted by GC/MS and GC. The Al-SBA-16 led to a higher catalytic conversion than SBA-16. Hydrocarbons (C_7 - C_{10}) were mainly produced by Al-SBA-16, whereas a much broader distribution of oil products (C_7 - C_{14}) was obtained by SBA-16. The Al-SBA-16 also showed high catalytic stability. The results of this study suggest that Al-SBA-16 has a high potential as a catalyst for degradation of waste plastics.

Key words: Polyethylene, SBA-16, Catalytic Degradation

INTRODUCTION

Given their diversity, relatively low cost, low density, and high formability, plastics have been used in a variety of applications. Owing to their low biodegradability and different chemical compositions, the mass consumption of plastics, however, has raised severe environmental issues when they are disposed by incineration or landfill. Over the last few decades, much attention has been given to the recycling of plastics as an alternative to disposal and management. There are two main routes in waste plastic recycling: mechanical reprocessing and thermal and/or catalytic degradation into gas and liquid products that can be used as fuels or chemicals of value. A drawback of mechanical reprocessing is that the quality of the products is usually low [1]. Thermal/catalytic degradation has been applied successfully, but only towards recovering monomers from certain kinds of polymers, such as polystyrene (PS), polytetrafluoroethylene (PTFE), poly(methylmethacrylate) (PMMA), and polyethyleneterephthalate (PET), because of its high energy consumption [2,3]. Another disadvantage of thermal degradation is the low selectivity towards desired products [4].

Catalytic degradation has several advantages over thermal degradation: lower energy consumption stemming from lower reaction temperature, faster cracking, lower residence time, high selectivity for required products that can be obtained by selecting catalysts and process conditions carefully, and inhibition of undesired product generation (chlorinated hydrocarbons) [4]. In the catalytic degradation of plastics, efforts have been made to utilize a variety of catalysts, including zeolite, silica-alumina, alumina, fresh and spent FCC catalysts, montmorillonite, and mesoporous materials [1,5-12]. In

particular, mesoporous materials have high accessibility to the inner active sites of bulky substances due to their large pore openings. For example, MCM-41, SBA-15, and MCM-48 have been applied to catalytic degradation of polyethylene. Moreover, SBA-16 is also expected to possess high activity in the catalytic degradation of plastics given its super-large cage, high surface area, and high thermal stability. In particular, its three-dimensional channel connectivity provides more favorable mass transfer kinetics than the unidirectional pore structures of other hexagonal mesoporous materials. To the best of the authors' knowledge, SBA-16 is utilized for the first time for the catalytic degradation of waste plastics.

In this paper, a feasibility study on the use of SBA-16 for the degradation of polyethylene is reported. The performance of SBA-16 towards two kinds of polyethylenes, high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE), is evaluated. The effect of the acidity of SBA-16 on the degradation efficiency is also discussed.

EXPERIMENTAL

1. Catalyst Synthesis

Mesoporous silica SBA-16 materials with cubic *Im-3m* structure were synthesized according to the procedure described elsewhere [13]. Briefly, poly(alkylene oxide)-type triblock copolymer, F127 ($EO_{106}PO_{70}EO_{106}$, MW=12,600, Sigma) were dissolved in aqueous HCl solution. Tetraethyl orthosilicate (TEOS, 98%) was added to the solution at 308 K, and magnetic stirring was continued for 15 min at the same temperature. The molar composition of the mixture was as follows: F127/TEOS/HCl/ H_2O =0.0040/1.0/4.0/130. This mixture was kept under static conditions in an oven for 24 h at the same temperature. Subsequently, the mixture was placed in an oven at 373 K for 24 h. After such hydrothermal aging, the solid product was re-

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covered by filtration and dried at 373 K without washing. The samples were then washed with ethanol, dried in an oven at 373 K and calcined at 823 K. SBA-15 was synthesized according the procedure described in the literature [14]. The Al incorporation was carried out with ethanolic solution of AlCl_3 ($\text{Si}/\text{Al}=30, 60$). After the solvent ethanol was completely evaporated in a rotary evaporator, the samples were calcined in air at 823 K. The Al-incorporating samples are denoted by Al-SBA-16 or Al-SBA-15.

2. Characterization

Mesostructures of the synthesized materials were identified by powder X-ray diffraction (XRD, Rigaku D/max-RC). All N_2 adsorption-desorption isotherms were obtained with a Micromeritics ASAP 2040 apparatus at a liquid N_2 temperature. The NH_3 -TPD profile was measured employing a TPD/TPR 2900 analyzer (Micromeritics Instrument Co.).

3. Materials and Thermogravimetric Analysis

The HDPE and LLDPE, both in powder form, were supplied from Samsung Total Co., Korea. Because thermogravimetric analysis can provide useful kinetic data about pyrolysis [15,16], the catalytic degradation kinetics of the polyethylene over the catalysts was evaluated using a thermogravimetric analyzer (TGA 2050, TA Instrument). Thermogravimetric analysis (TGA) was performed with 10.0 mg of a 1 : 1 sample:catalyst ratio (w/w) between 30 and 600 °C, with linear heating rates of 5, 10, and 20 °C/min, under a nitrogen atmosphere at a flow rate of 90 mL/min.

To test the extent of deactivation of Al-SBA-16 ($\text{Si}/\text{Al}=30$) and Al-SBA-15 ($\text{Si}/\text{Al}=30$), the catalyst (sample:catalyst ratio (w/w)=10 : 1) was applied five times to TGA, without regeneration of the spent catalyst during the TGA experiments.

4. Catalytic Degradation Reactions of Polyethylene

The catalytic degradation of polyethylene was also performed in a fixed bed reactor. A schematic diagram of the experimental apparatus is shown in Fig. 1. A well-mixed sample of polyethylene to catalyst (10 : 1 (w/w)) was charged into a U-type quartz reactor. The reactor was equipped with an external electronic heating furnace and heated at a rate of 50 °C/min to the reaction temperature (430 °C), which was then maintained for 2 h and continually monitored using a thermocouple in direct contact with the reaction mixture. The gaseous products at the reaction temperature were swept out from the reactor by a nitrogen stream and separated into liquid and gaseous fractions in a condenser cooled by a chiller. The liquid

fraction was collected from the bottom of the condenser and weighed. The effluent gas flow was continuously measured by a soap meter placed after the condenser, which was finally collected in a gasbag.

The oil and gaseous products were analyzed by gas chromatography/mass spectrometry (GC/MS (HP 5973)) and gas chromatography, equipped with flame ionization detection (GC-FID (ACME 6000, Young Lin Instrument Co., Ltd.), respectively. The columns used were an HP-5MS (30 m×0.25 mm×0.25 μm) capillary column for the GC/MS and an HP-plot $\text{Al}_2\text{O}_3/\text{KCl}$ (50 m×0.32 mm×8.0 μm) for the GC/FID, respectively.

RESULTS AND DISCUSSION

1. Characterization of SBA-16

The XRD pattern of synthesized SBA-16 is shown in Fig. 2, which could be identified as that of cubic SBA-16 with sharp (110) and small (200) reflections. The lattice parameter was calculated to be $a=13.3$ nm for the calcined sample (not shown), close to the value reported in the literature [17]. After the incorporation of Al species, XRD patterns of Al-SBA-16 with Si/Al ratio of 60 and 30 exhibited slight decrease of intensity of characteristic peaks (not shown), but still maintained the well-ordered patterns of Al-incorporated mesoporous silicas demonstrating the cubic SBA-16 structure. This result indicates that the cubic mesostructure was not destroyed by incorporation of alumina in the silica frameworks.

The nitrogen isotherms of all calcined samples showed the type IV behavior of cage-like pore structure with a hysteresis loop (Fig. 3). The desorption delay and curve steepness in the relative pressure range of 0.4-0.6 clearly showed the cage-like structure of the cubic mesostructure with relatively narrow constrictions of entrances [13]. As shown in Table 1, the SBA-16, Al-SBA-16 ($\text{Si}/\text{Al}=60$), and Al-SBA-16 ($\text{Si}/\text{Al}=30$) showed high BET surface areas of 791, 737, and 702 $\text{m}^2 \text{g}^{-1}$, and total pore volumes of 0.54, 0.5, and 0.48 $\text{cm}^3 \text{g}^{-1}$, respectively.

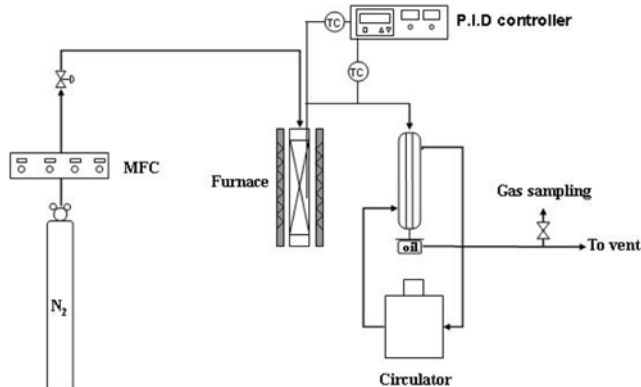


Fig. 1. Schematic diagram of the experimental apparatus.

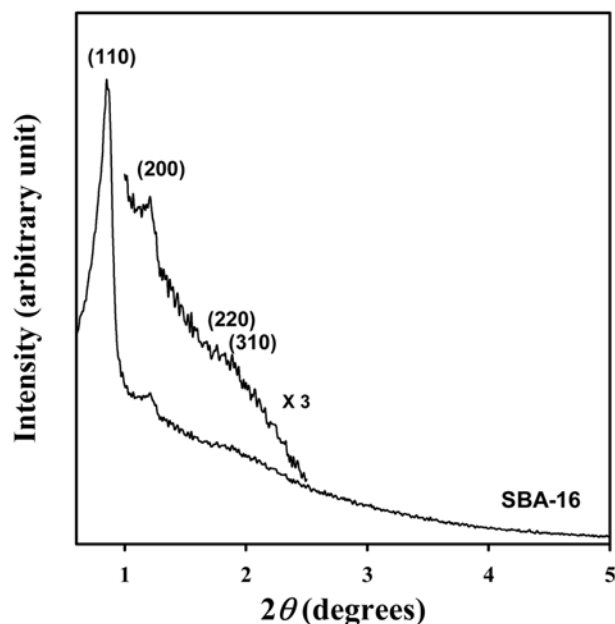


Fig. 2. XRD patterns of synthesized SBA-16 catalyst.

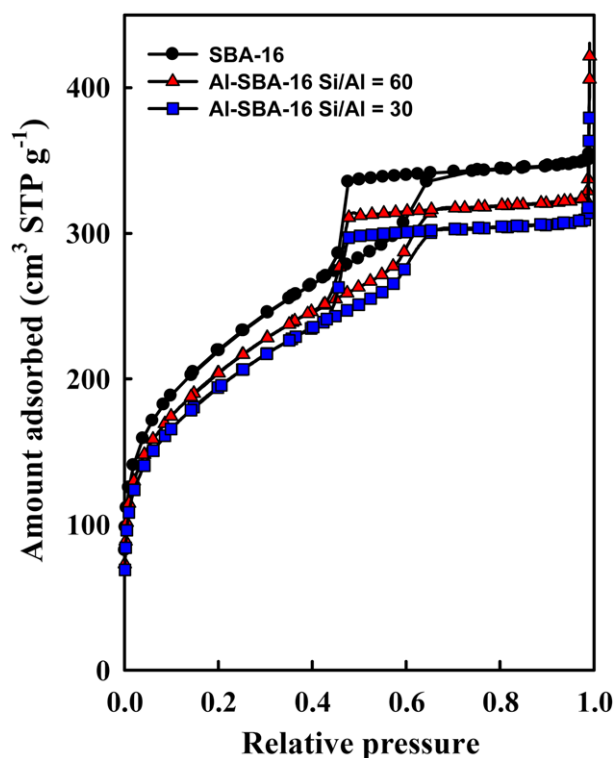


Fig. 3. N₂ adsorption/desorption isotherms of SBA-16 catalysts.

Table 1. Physicochemical characteristics of the SBA-16 catalysts

Sample	Bulk Si/Al ratio	Textural properties		
		BET (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
SBA-16		791	0.54	5.1
Al-SBA-16	60	737	0.50	5.1
Al-SBA-16	30	702	0.48	5.1

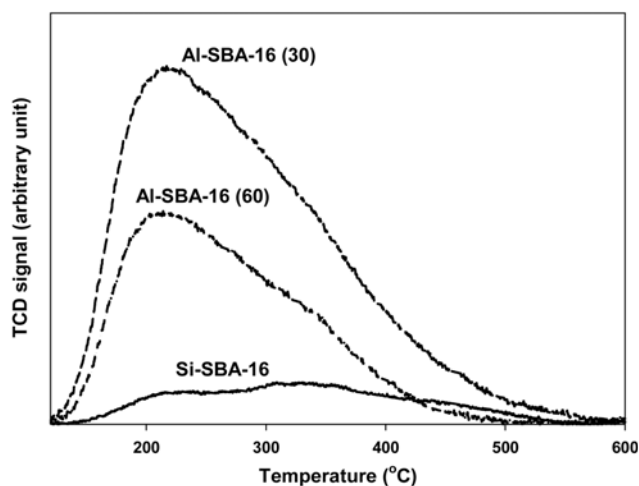


Fig. 4. NH₃-TPD curves of SBA-16 catalysts.

It can be seen in NH₃-TPD results (Fig. 4) that the incorporation of aluminum into the SBA-16 generated more acid sites required

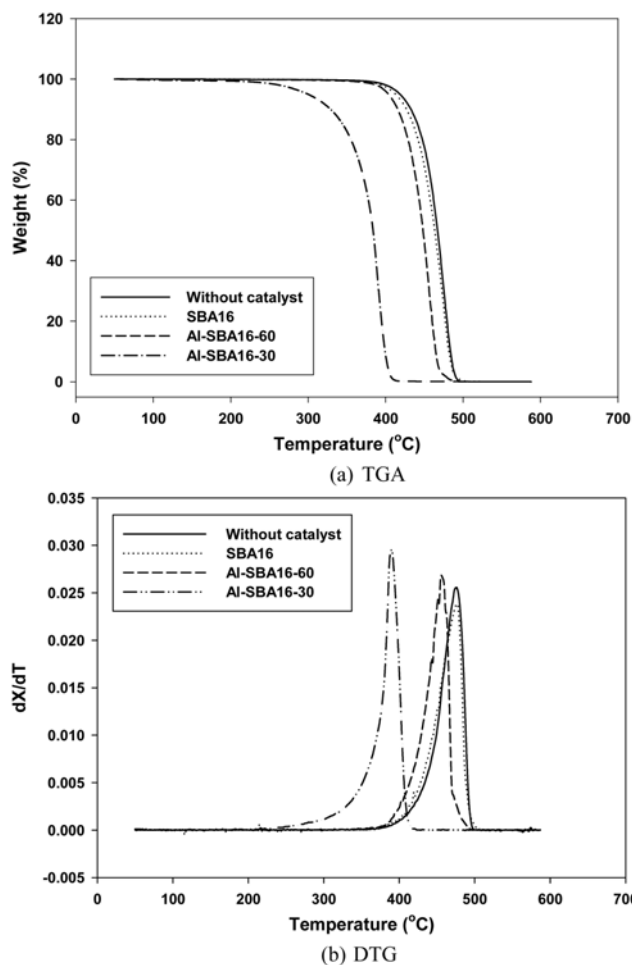


Fig. 5. TGA and DTG curves of LLDPE degradation on SBA-16 catalysts with a heating rate of 10 K/min.

for acid-catalyzed reactions, whereas pure silica materials did not possess enough acidity or reactivity to be used as a catalyst. In addition, Al-SBA-16 (Si/Al=30) was shown to have more acid sites than Al-SBA-16 (Si/Al=60).

2. Catalytic Degradation

The TG and DTG curves for the thermal and catalytic degradation of LLDPE over the SBA-16 are shown in Fig. 5. Compared to thermal degradation, the degradation temperature was reduced slightly by addition of SBA-16 in catalytic degradation. However, the addition of Al-SBA-16 considerably decreased the degradation temperature. In particular, the addition of Al-SBA-16 with a Si/Al ratio of 30 caused the largest reduction in degradation temperature. As shown in Fig. 4, this is attributed to a large number of acid sites that can be regarded as the active sites for the catalytic degradation. The TG and DTG curves for HDPE degradation showed similar tendencies (not shown).

The conversion and product composition results for PE degradation are shown in Table 2. The degradation efficiency of Al-SBA-16 was much higher than that of SBA-16. In particular, Al-SBA-16 (Si/Al=30) showed an activity higher than Al SBA-16 (Si/Al=60), which can be attributed to the larger number of acid sites in Al-SBA-16 (Si/Al=30). Table 3 shows the chemical composition, sorted by the number of carbons in the molecules, of gaseous products obtained

Table 2. Product distribution of polyethylene degradation

Catalyst		SBA-16	Al-SBA-16 (Si/Al=60)	Al-SBA-16 (Si/Al=30)
HDPE	Conversion (%)	49.6	87.2	96.4
	Yield (wt%)			
	Oil	43.3	76.4	75.8
	Gas	6.3	10.8	20.6
LLDPE	Conversion (%)	66.2	91.4	99.2
	Yield (wt%)			
	Oil	60.7	80.4	80.6
	Gas	5.5	11.0	18.6

Temperature: 430 °C

Sample/catalyst (w/w): 10/1

Table 3. Product distribution of gas

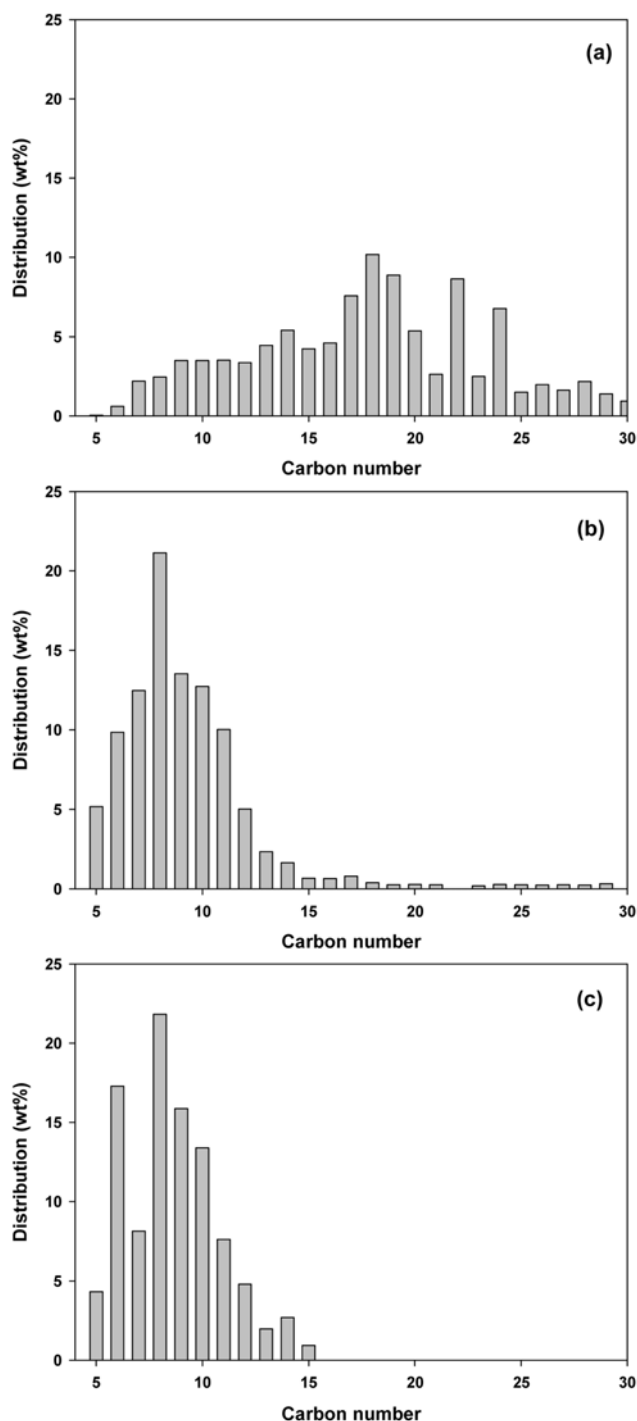
Catalyst		SBA-16	Al-SBA-16 (Si/Al=60)	Al-SBA-16 (Si/Al=30)
HDPE	Distribution (wt%)			
	CH ₄	0.2	0.1	0.1
	C ₂ H ₄	0.4	0.1	0.2
	C ₂ H ₆	0.6	0.1	0.1
	C ₃ H ₆	1.5	3.4	5.2
	C ₃ H ₈	1.2	0.3	0.6
	C ₄ H ₈ (<i>c-,t-,n-</i>)	1.3	3.1	7.0
	<i>i</i> -C ₄ H ₈	0.2	2.8	4.0
	C ₄ H ₁₀ (<i>i-,n-</i>)	0.9	0.9	3.4
	Σparaffins	2.9	1.4	4.2
LLDPE	Σolefins	3.4	9.4	16.4
	Distribution (wt%)			
	CH ₄	0.3	0.1	0.1
	C ₂ H ₄	0.4	0.2	0.1
	C ₂ H ₆	0.9	0.3	0.1
	C ₃ H ₆	1.1	2.8	4.4
	C ₃ H ₈	0.9	0.4	0.5
	C ₄ H ₈ (<i>c-,t-,n-</i>)	1.1	3.6	6.5
	<i>i</i> -C ₄ H ₈	0.1	2.8	3.4
	C ₄ H ₁₀ (<i>i-,n-</i>)	0.7	0.8	3.5
	Σparaffins	2.8	1.6	4.2
	Σolefins	2.7	9.4	14.4

Temperature: 430 °C

Sample/catalyst (w/w): 10/1

by the catalytic cracking of polyethylenes. The Al-SBA-16 led to very high yields of C₃-C₄ hydrocarbons, most of which are olefins of value. Because of the weak acidity of Al-SBA-16 catalysts (Fig. 4), the possibility of hydrogen transfer from olefin to paraffin is low. Moreover, it may be very difficult that additional polymerization of produced olefins can occur on weak acid sites. Meanwhile, degradation of HDPE over FER (Si/Al=10) with high acid sites resulted in higher paraffin yield (paraffin/olefin=1) [5]. Therefore, Al-SBA-16 (Si/Al=30), having the largest amount of acid sites, led to the highest yield of olefins.

Regarding the liquid products, SBA-16 showed a broad carbon number distribution, up to C₂₄ hydrocarbons due to random crack-

**Fig. 6. Product distribution of oil by catalytic conversion of HDPE over SBA-16 catalysts. (a) SBA-16 (b) Al-SBA-16 (Si/Al=60) (c) Al-SBA-16 (Si/Al=30).**

ing reactions (Fig. 6) [18]. In the case of catalytic cracking with Al-SBA-16, however, high selectivity to light hydrocarbons (C₆-C₁₂), in the range of gasoline and diesel oils, was observed. This selectivity pattern is ascribed to the weak acid sites, which led to a carbocationic end-chain cracking mechanism, mostly due to a β-scission reaction [18]. Furthermore, the fully accessible mesoporous structure of Al-SBA-16 may have contributed to the high selectivity of light hydrocarbons.

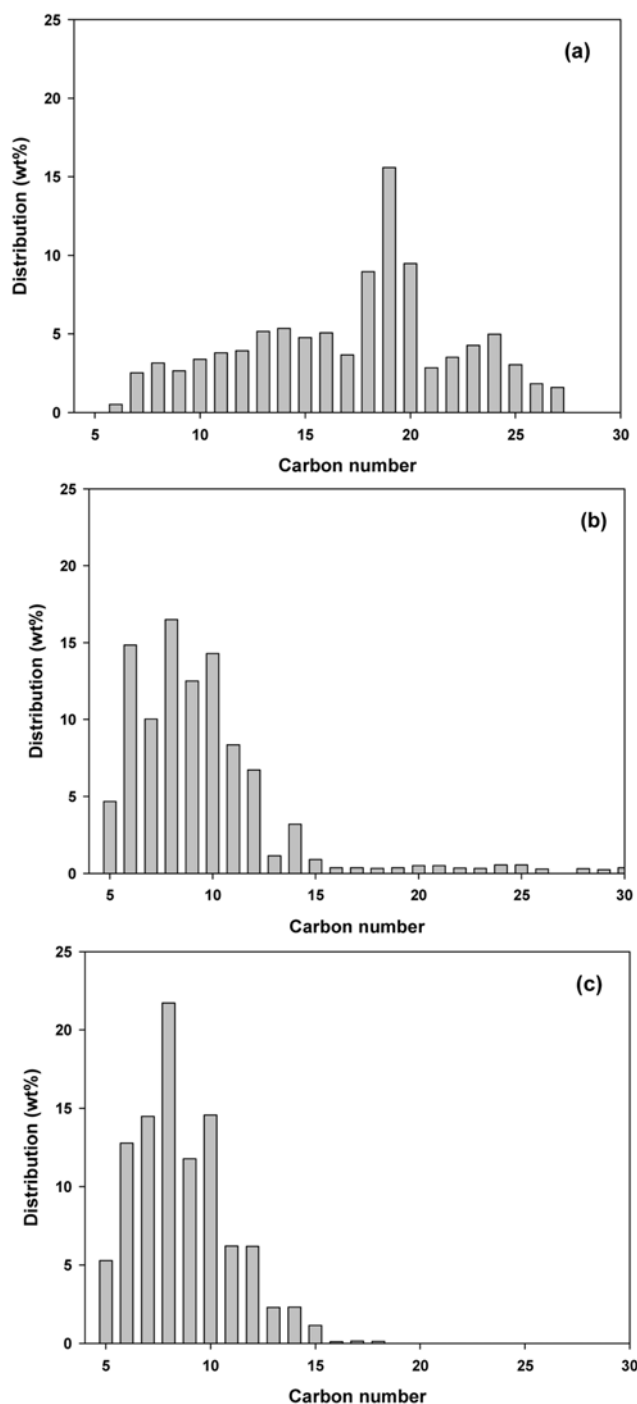


Fig. 7. Product distribution of oil by catalytic conversion of LLDPE over SBA-16 catalysts. (a) SBA-16 (b) Al-SBA-16 (Si/Al=60) (c) Al-SBA-16 (Si/Al=30).

To test the catalytic stability, repetitive TGA experiments were performed, in which the same experiments were repeated five times without any regeneration of the catalyst. In this experiment, Al-SBA-16 (30) was compared with Al-SBA-15 (30) because Al-SBA-15 is known to be an effective catalyst that degrades polyethylene and has different pore structure with Al-SBA-16. After five iterations, ΔT (temperature difference between 1st reaction and 5th reaction) was below 5 °C for the Al-SBA-16 (30). Because Al-SBA-16 has

a three-dimensional pore structure, the catalytic activity was conserved during the repetitive experiments. Nevertheless, for the Al-SBA-15 (Si/Al=30), which is known to be an effective catalyst that degrades polyethylene, the final degradation temperature was shifted by 70 °C to a higher temperature. This implies that catalytic activity of Al-SBA-15 having one-dimensional pore structure decreased significantly. The coke amounts of Al-SBA-16 and Al-SBA-15 were also compared. The Al-SBA-16 contained less coke (8.4 wt%) than Al-SBA-15 (11.9 wt%), indicating a higher resistance of Al-SBA-16 to deactivation. These results suggest that Al-SBA-16 has a higher potential as a catalyst for polyethylene degradation than Al-SBA-15.

CONCLUSIONS

The catalytic performance of Al-SBA-16 toward the degradation of polyethylenes was evaluated experimentally. The conversion of polyethylenes was enhanced significantly by the addition of Al-SBA-16. The high catalytic performance of Al-SBA-16 (Si/Al=30), compared to other catalysts tested, is attributed to its large number of weak acid sites.

Given the high yields of valuable olefins and gasoline/diesel range oils and overall resistance to coke formation, Al-SBA-16 is contended to possess high potential as a catalyst for polyethylene degradation.

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