

Jeong-Geol Na · Byung-Hwan Jeong · Soo Hyun Chung
Seong-Soo Kim

Pyrolysis of low-density polyethylene using synthetic catalysts produced from fly ash

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Abstract Catalytic pyrolysis of low-density polyethylene (LDPE) was investigated using various fly ash-derived silica–alumina catalysts (FSAs). FSAs were prepared by a simple activation method that basically includes NaOH treatment of fly ash by a fusion method, followed by an aging process. A series of LDPE pyrolysis experiments was conducted and the catalytic performance of FSAs was assessed in terms of the degradation temperature and the simulated boiling point distribution of the liquid products. The effects of synthesis conditions such as NaOH/fly ash weight ratio and aging time were examined by X-ray diffractometer (XRD), Brunauer-Emmett-Teller (BET) surface area analyzer, and scanning electron microscope to clarify the controlling factors affecting the catalytic activity. To obtain catalyst with high activity, it is necessary to produce sufficient silica and alumina species that can be easily co-precipitated into solid acid catalyst by destruction of the fly ash structure and to optimize the activation time for catalyst synthesis to prevent the transformation into inactive phases. The catalytic performance of FSA obtained from optimal conditions was equivalent to that of commercial catalysts, demonstrating the effectiveness of the catalyst.

Key words Fly ash-derived silica–alumina catalyst · NaOH fusion · Catalytic pyrolysis · Low-density polyethylene

Introduction

Among various technologies for waste plastic treatment, pyrolysis is considered one of the most promising because waste plastics can be upgraded into valuable fuel oils and chemicals by this technology. Pyrolysis can be conducted with or without a catalyst.^{1–10} The advantages of catalytic pyrolysis against thermal pyrolysis are lower degradation

temperatures and a narrower molecular size distribution of products.^{3,4} As a result of these advantages, catalytic pyrolysis has been an attractive research topic in the area of waste recycling technology. However, economic efficiency still remains a problem because commercial catalysts are generally expensive and have a relatively short life in the pyrolysis process. Much effort has been expended to develop a low-price catalyst.^{3,5–7}

This study was aimed at developing a low-price catalyst that is suitable for pyrolysis of waste plastics. Fly ash, which is the waste material generated from coal-fired power plants, was used as the source of silica and alumina for solid acid catalysts. The amount of fly ash generated in Korea was about 3.6 million tons in 1998 and its annual generation has been rapidly increasing.¹¹ The primary use of fly ash has been in concrete and cement manufacturing. However, many researchers have recently synthesized zeolites from fly ash and applied these fly ash-derived zeolites as cation exchangers for the removal of heavy metals from wastewater and also as molecular sieves for the separation and recovery of gases such as CO₂, SO₂, and NH₃.^{12–14}

In our previous work,^{5–7} fly ash-derived catalysts containing faujasitic zeolites were developed for the pyrolysis of polypropylene. However, it was shown that their catalytic activity was too weak to be applied in the pyrolysis of LDPE. Fly ash-derived zeolites (FAZs) are composed of not only faujasitic materials appropriate for pyrolysis, but also by-products such as NaP1 zeolites and unreacted fly ash. Moreover, the zeolite type and thus its catalytic activity depends on the type of fly ash used.¹² The result is that it is difficult to obtain catalysts that yield reproducibility of results.

In this study, amorphous silica–alumina catalysts (FSAs) were synthesized by activation of fly ash with NaOH. The factors affecting the performance of the FSAs, i.e., NaOH/fly ash weight ratio and activation time, were investigated. A series of LDPE pyrolysis experiments was conducted to evaluate the performance of the FSAs. The performance of these catalysts for LDPE pyrolysis was assessed in terms of the degradation temperature and simulated boiling point distribution of the liquid products. The

J.-G. Na · B.-H. Jeong · S.H. Chung (✉) · S.-S. Kim
Energy Conversion Research Department, Korea Institute of Energy
Research, Daejeon 305-343, Korea
Tel. +82-42-860-3638; Fax +82-42-860-3134
e-mail: chung@kier.re.kr

physicochemical properties of the FSAs were also characterized and related to their catalytic performance for the pyrolysis of LDPE.

Experimental

Synthesis of FSAs

The fly ash powder with an average diameter of 20–30 μm used in this study was supplied by Boryung coal-fired power plants in Korea. Table 1 shows the chemical composition of the fly ash used. The fly ash was composed of SiO₂ and Al₂O₃ with minor amounts of Fe₂O₃ and CaO. FSAs were synthesized by dissolution of silica and alumina from fly ash, followed by co-precipitation of the dissolved ions.

Fly ash (100 g) was mixed with different amounts of NaOH (70, 120, and 170 g). This mixture was fused in air at 600 °C for 1.5 h. The fused product was cooled and dissolved in distilled water with a solid/liquid ratio of 0.2 (w/w), followed by an activation process with agitation in a reactor at room temperature for different periods (8, 16, and 32 h). The synthesis conditions are summarized in Table 2. The resulting materials were separated into a solid phase and waste solutions by filtration. The solid phase was washed several times with 1 M NH₄Cl and then dried at 60 °C for 24 h. At the end of the process, solid acid catalysts were prepared by calcining at 500 °C for 4 h in air.

Table 1. Chemical composition of the fly ash used in this study

Component	Weight (%)
SiO ₂	53.56
Al ₂ O ₃	27.71
Fe ₂ O ₃	5.53
MgO	0.91
CaO	4.50
K ₂ O	0.94
Na ₂ O	0.37
Others	6.48
Ignition loss	5.88

Table 2. Reaction conditions for fly ash-derived silica–alumina catalyst (FSA) synthesis

Catalyst	Synthesis conditions	
	NaOH/fly ash (w/w)	Activation time (h)
FSA(0.7)		
FSA(0.7-8)	0.7	8
FSA(0.7-16)	0.7	16
FSA(0.7-32)	0.7	32
FSA(1.2)		
FSA(1.2-8)	1.2	8
FSA(1.2-16)	1.2	16
FSA(1.2-32)	1.2	32
FSA(1.7)		
FSA(1.7-8)	1.7	8
FSA(1.7-16)	1.7	16
FSA(1.7-32)	1.7	32

Characterization of FSAs

To examine the crystallinity of the synthesized catalysts, X-ray diffraction (XRD) patterns were identified by a Phillips X'Pert-MPD diffractometer (Phillips Electron Optics, Eindhoven, the Netherlands) using CuK α radiation as a source of X-rays in the range 3°–60°. The specific surface area and the pore volume were measured by Brunauer-Emmett-Teller (BET) apparatus (Quantasorb sorption system, Quantachrome, Boynton Beach, FL, USA). The morphology of the samples was observed by a scanning electron microscope (SEM, Model XL 30, Phillips Electron Optics).

Degradation of LDPE and analysis of the liquid products

Thermal and catalytic pyrolysis of LDPE was carried out in a thermogravimetric analyzer (TGA) under atmospheric pressure. LDPE pellets with an average size of 3 mm were purchased from SK Corporation (Seoul, Korea). The physical properties of the LDPE pellets were a melting point of 110 °C, a melt flow index of 0.3 g/10 min, and a density of 0.92 g/cm³.

To examine the shift of degradation temperature and the liquid product distribution on using the catalyst, a magnetic suspension balance (MSB) thermogravimetric analyzer (Rubotherm, Bochum, Germany) was used (Fig. 1). LDPE pellets (5 g) with or without catalyst (LDPE:catalyst = 10:1) was heated up to 600 °C with a linear heating rate of 5 °C/min in a N₂ atmosphere and the weight loss of the LDPE was recorded. Nitrogen was used as a carrier gas at a flow rate of 60 ml/min.

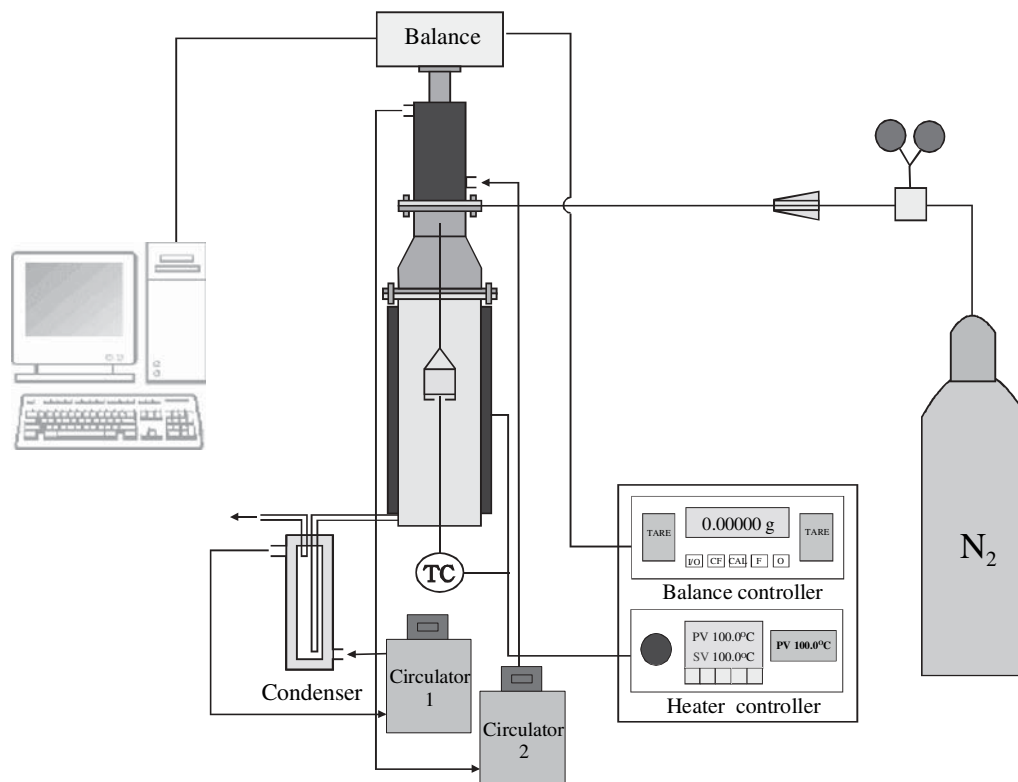
During the pyrolysis experiments, the gaseous product was vented to the atmosphere and the liquid vapor product was recovered as condensed pyrolysis oil (liquid product). The distribution of the boiling point range of the liquid products diluted with carbon disulfide was determined by gas chromatography (HP6890 GC; Hewlett-Packard, Palo Alto, CA, USA) using a simulated distillation method (SIMDIS) as described in ASTM D2887-93.¹⁵

Results and discussion

Catalytic performance of FSAs

To investigate the catalytic activity of FSAs, thermal and catalytic pyrolysis of LDPE was carried out in a TGA. Figure 2a–d shows the comparative catalytic performance of FSAs in terms of changes in the degradation temperature. The optimal activation time for catalyst synthesis was found to be 0.7 h. LDPE degradation by FSA(0.7-16) and FSA(0.7-32) started earlier than for FSA(0.7-8); however, a decrease in the activity of FSA(0.7-32) was observed after 60% LDPE degradation. From these results, FSA(0.7-16) was identified as the best catalyst in the FSA(0.7) group. During the degradation of LDPE by FSA(1.2) and FSA(1.7), a slight decrease in catalytic activity was observed

Fig. 1. Magnetic suspension balance (MSB)



with the activation time for catalyst synthesis. As shown in Fig. 2b, degradation with FSA(1.2-8) started earlier than for FSA(1.2-16) and FSA(1.2-32). FSA(1.7-8) could degrade LDPE at lower temperatures than for FSA(1.7-16) or FSA(1.7-32), the pattern being similar to that for the FSA(1.2) group (Fig. 2c). Therefore, it was concluded that FSA(1.2-8) and FSA(1.7-8) had the best catalytic activity among the FSA(1.2) and FSA(1.7) catalyst group, respectively.

The reason the catalytic activity did not increase with catalyst activation time might have been that the transformation of FSAs into inactive phases increasingly occurred with time. In fact, the phase transformation of NaOH-fused fly ash samples with time even at low temperatures has been observed in previous reports,^{6,7,14} the implication being that the determination of activation time is important to obtain a good catalyst.

Figure 2d shows the weight loss patterns on LDPE pyrolysis with FSA(0.7-16), FSA(1.2-8), and FSA(1.7-8), which were selected as the best catalysts in each catalyst group. Catalysts synthesized with a high NaOH/fly ash weight ratio [FSA(1.2-8) and FSA(1.7-8)] showed better catalytic performance in degrading LDPE compared to FSA(0.7-16), which employed a lower NaOH/fly ash weight ratio. Although FSA(1.2-8) and FSA(1.7-8) exhibited similar trends of degradation, FSA(1.2-8) would be preferable for waste plastics recycling in terms of the production cost of catalyst because of the lower consumption of NaOH. Therefore, FSA(1.2-8) was selected for further tests.

To evaluate the usefulness of FSA(1.2-8), its catalytic activity was compared with that of commercial catalysts [HY(5.1) zeolite (Si/Al = 5.1, Zeolyst, Valley Forge, PA, USA) and silica–alumina catalyst (Sigma, St. Louis, MO, USA)]. Figure 2e illustrates the weight loss patterns on LDPE pyrolysis with the above three catalysts and without a catalyst. All the catalysts achieve a reduction in the temperature for a given conversion level compared to thermal pyrolysis. FSA(1.2-8) lowered the LDPE degradation temperature by more than 50°C compared with thermal degradation. Moreover, the catalytic performance of FSA was comparable to that of HY(5.1) commercial zeolite catalyst. On pyrolysis with HY(5.1), LDPE degradation began at a lower temperature, but was retarded as time progressed, indicating a loss of catalytic activity. As discussed elsewhere,¹⁰ zeolite-Y, including HY(5.1), is relatively weak in terms of coke formation because of the large pore openings, thus coke formation may be the main reason for the reduced activity in the latter stages of pyrolysis.

FSA(1.2-8) requires a higher degradation temperature than does commercial silica–alumina (SA) catalyst. Although FSA(1.2-8) is inferior to SA catalyst in terms of its catalytic activity, it is expected that low production costs will help FSA(1.2-8), which is made from the waste generated in coal-fired power plants, compete with SA catalyst. It is possible to obtain the desirable catalytic activity by increasing catalyst loading; accordingly, FSA(1.2-8) could be a good candidate for catalytic use in the recycling of waste LDPE.

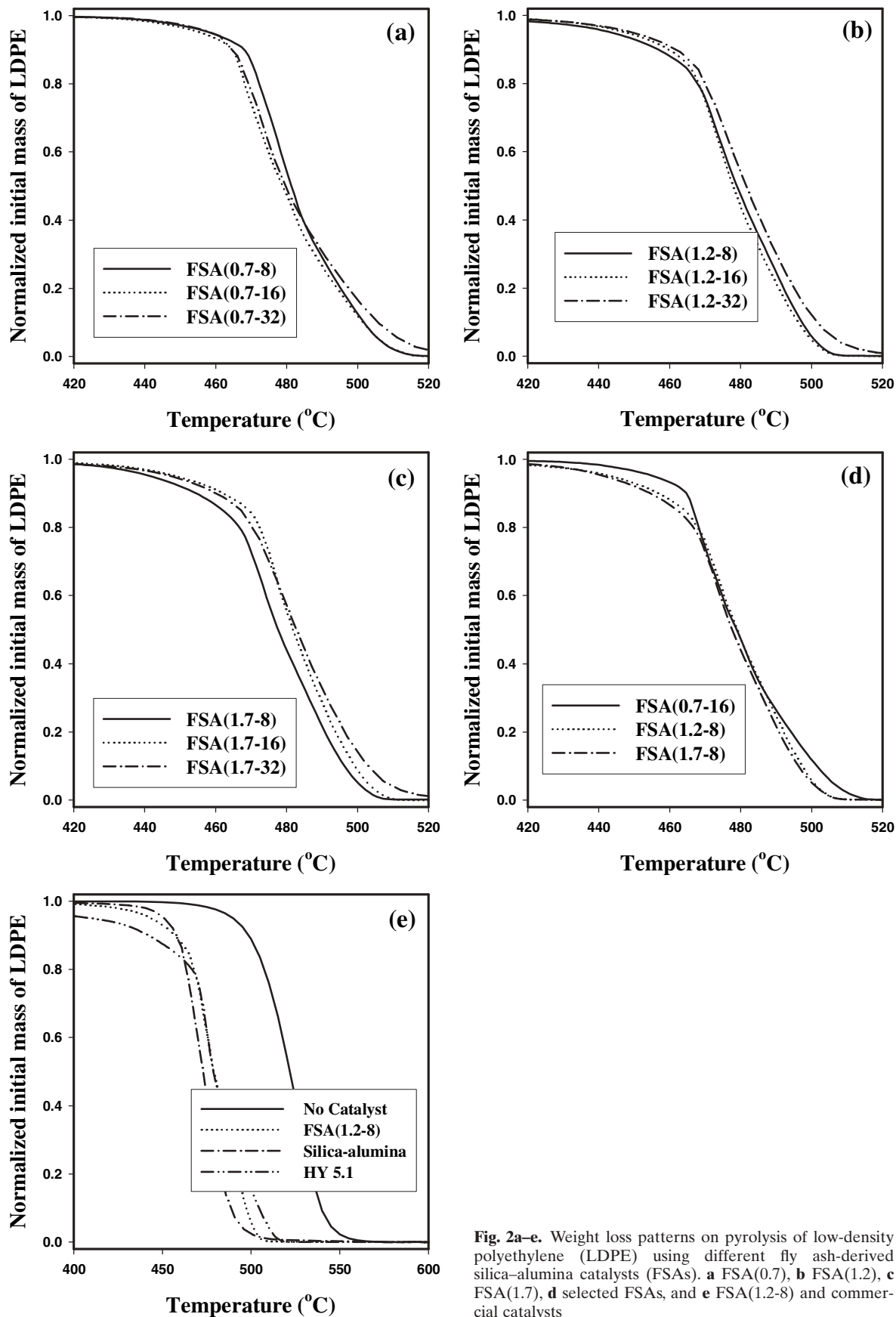


Fig. 2a–e. Weight loss patterns on pyrolysis of low-density polyethylene (LDPE) using different fly ash-derived silica-alumina catalysts (FSAs). **a** FSA(0.7), **b** FSA(1.2), **c** FSA(1.7), **d** selected FSAs, and **e** FSA(1.2-8) and commercial catalysts

Figure 3 shows the boiling point distribution of the liquid products of pyrolysis and also supports the catalytic efficiency of FSA(1.2-8). The boiling point distribution of the liquid product of pyrolysis with FSA(1.2-8) is in a lower temperature region than that of the product by thermal pyrolysis, and 70% of liquid products from LDPE pyrolysis

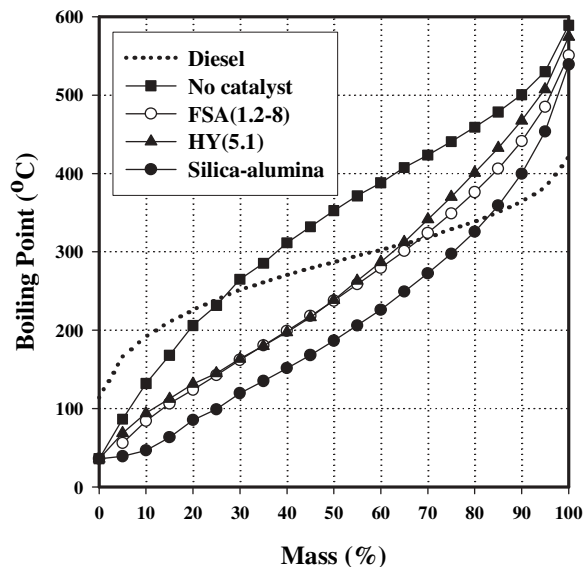


Fig. 3. Boiling point distribution of the liquid products obtained from the pyrolysis of LDPE using different catalysts

with FSA(1.2-8) had lower boiling points than diesel, indicating the high quality of the oil. The oil produced on catalysis with FSA(1.2-8) is comparable to that produced with HY zeolite and higher quality than that of SA catalyst. These results are consistent with the degradation temperatures obtained by TGA. Although the distribution of the liquid product for HY(5.1) is similar to that of FSA(1.2-8), waxy compounds and light oil were concurrently observed in the liquid product from HY(5.1) zeolite. It seems that the waxy compounds were generated on the loss of catalytic activity, whereas the light oil was mainly produced in the early stage of the pyrolysis.

Characterization of FSAs

FSAs showed different catalytic activity with different NaOH/fly ash weight ratios, and so these catalysts were characterized in more detail. Table 3 shows the BET surface area and pore volume of FSA(0.7-16), FSA(1.2-8), and FSA(1.7-16).

Figure 4a shows the XRD patterns of FSAs. FSA(1.2-8) and FSA(1.7-8) showed their amorphous features resulting from the transformation of fly ash, whereas unreacted quartz was observed in FSA(0.7-16). The BET surface area and pore volume also explain the relative efficiencies of the catalysts; as shown in Table 3, FSA(1.2-8) has the largest BET surface area and pore volume, followed by FSA(1.7-8) and FSA(0.7-16).

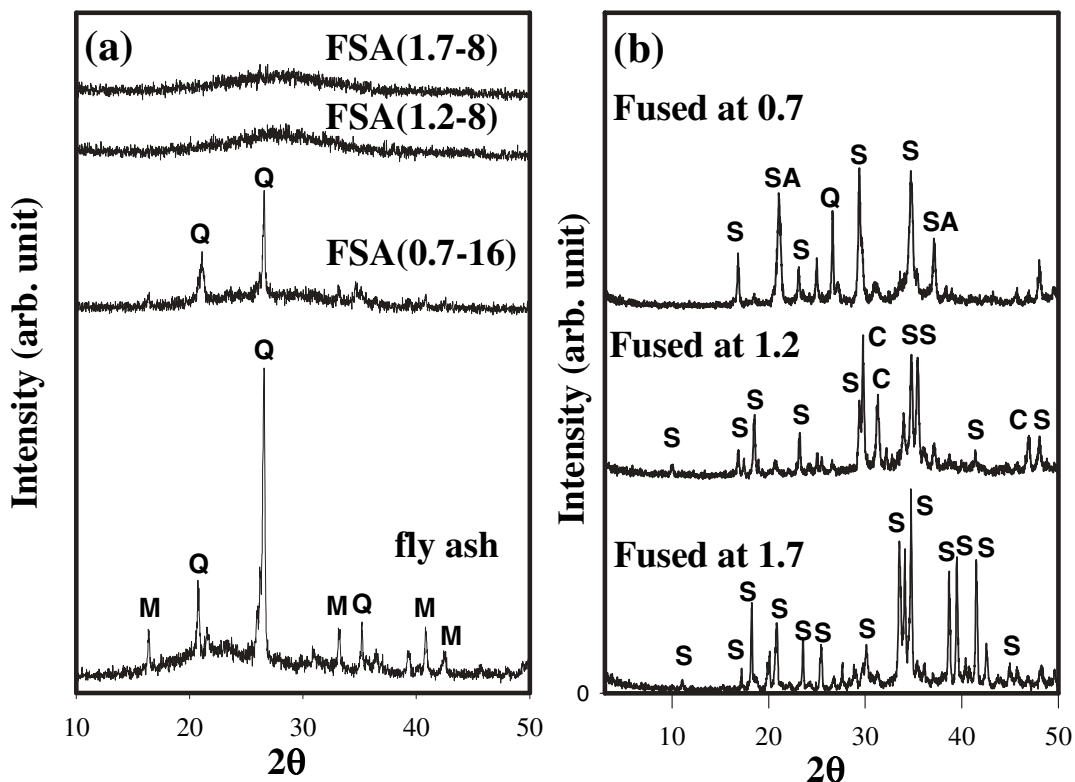
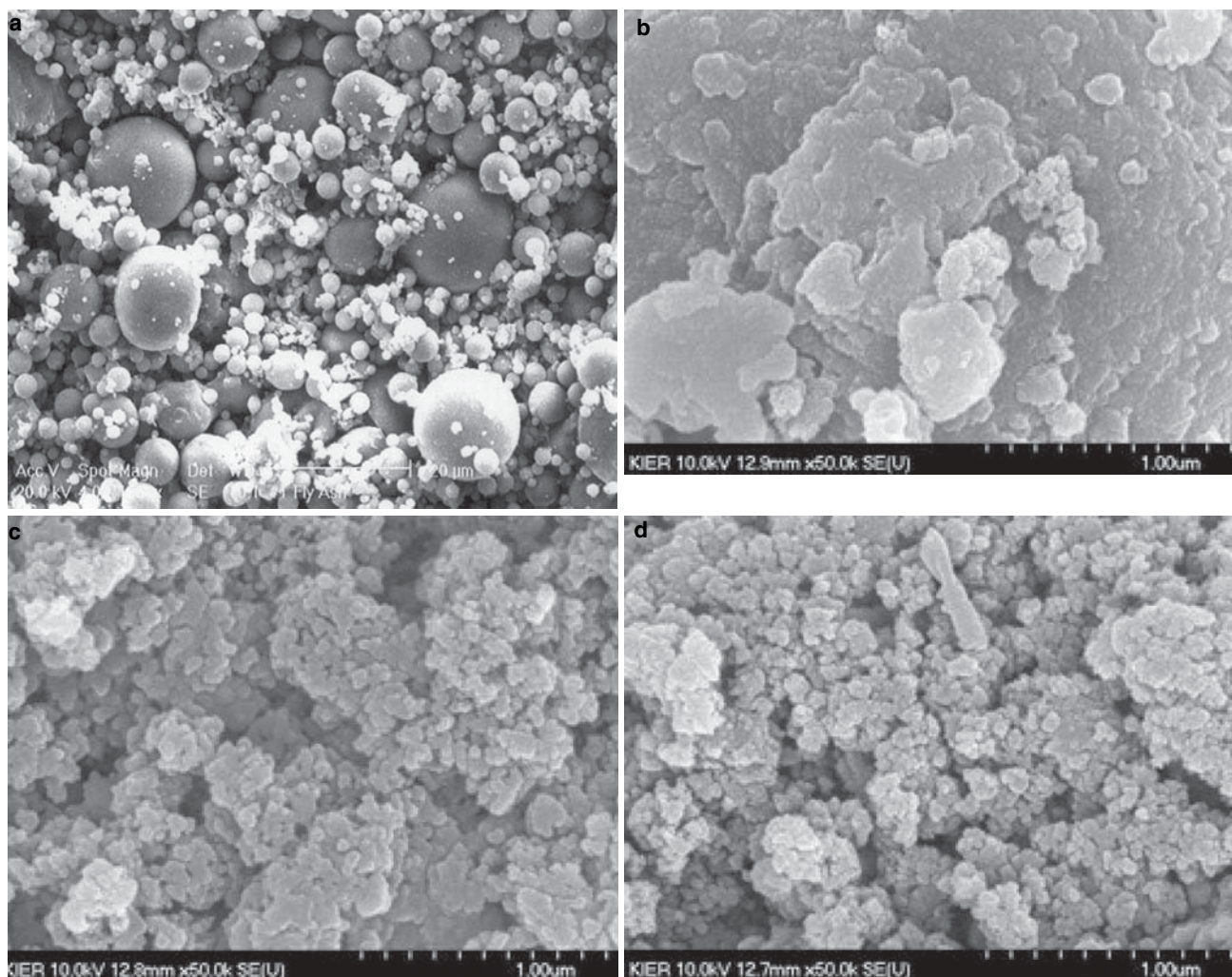


Fig. 4. X-ray diffraction patterns of **a** FSAs and **b** fused fly ashes. *Q*, quartz; *M*, mullite; *S*, sodium silicate; *SA*, sodium aluminum silicate; *C*, calcite

Table 3. BET surface areas, pore volumes, and average pore diameter of FSAs

Catalyst	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
FSA(0.7-16)	41.89	0.1588	15.17
FSA(1.2-8)	125.69	0.4901	15.60
FSA(1.7-8)	107.42	0.4814	17.93

BET, Brunauer-Emmett-Teller

**Fig. 5.** Scanning electron microscope images of **a** fly ash, **b** FSA(0.7-16), **c** FSA(1.2-8), and **d** FSA(1.7-8)

SEM images of FSAs, as shown in Fig. 5, show the morphology of the synthesized catalysts more clearly. In the SEM images of samples of FSA(1.2-8) and FSA(1.7-8), amorphous clusters were definitely observed, whereas relatively smooth surfaces were observed for FSA(0.7-16), probably to the result of less phase transformation, and this finding supports the results of XRD analysis.

To achieve a high level of activation, it is necessary to produce silica and alumina species that can be easily and sufficiently dissolved in water.¹⁴ As shown in Fig. 4b, significant amounts of sodium silicates were formed by NaOH

fusion at high fusion ratios (1.2 and 1.7), whereas some quartz still remained unreacted in the sample with a low fusion ratio (0.7). As a result, the species required for catalyst synthesis were not abundant using a low fusion ratio of 0.7, leading to a low efficiency for activation.

The BET surface area of FSA(1.2-8), 125.69 m²/g, is much smaller than that of commercial amorphous SA catalyst, which is generally as large as 500–600 m²/g. This is because the FSAs synthesized in this study are actually a mixture of catalysts and impurities rather than a high-purity catalyst, and FSA synthesis took place on the surface, primarily. As

a result, the performance of FSA(1.2-8) for the pyrolysis of LDPE was lower than that of commercial SA catalyst in terms of degradation temperature and the liquid product distribution.

Conclusions

Fly ash-derived amorphous silica–alumina catalysts for LDPE pyrolysis were synthesized easily and inexpensively by the fusion of fly ash with NaOH, followed by activation by co-precipitation. Synthesis parameters such as the NaOH/fly ash weight ratio and activation time had effects on the performance achieved by the catalysts. FSA(1.2-8) synthesized with an NaOH/fly ash weight ratio of 1.2 and an activation time of 8 h showed the best performance in terms of catalytic activity and production cost. The catalytic performance of FSA(1.2-8) was comparable with that of commercial catalysts and it was concluded that FSA could be a good candidate for catalytic use in the recycling of waste plastics.

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