



# Effect of acidity of solid acid catalysts during non-oxidative thermal decomposition of LDPE

Dipali P. Upare<sup>1</sup> · Chul Wee Lee<sup>1</sup> · Don Keun Lee<sup>1</sup> · Young Soo Kang<sup>1</sup>

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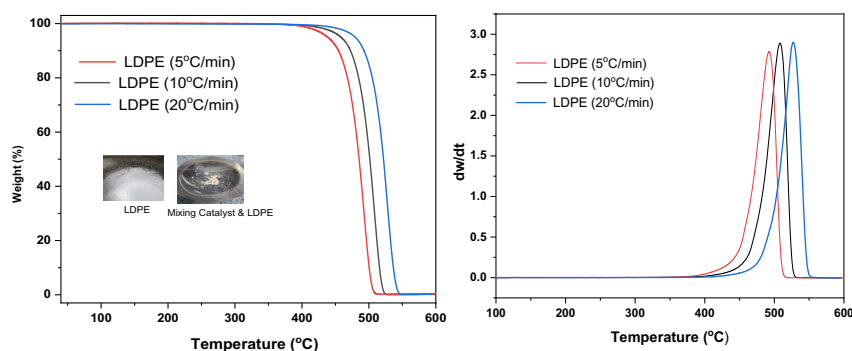
## Abstract

Thermal decomposition of low-density polyethylene (LDPE) was monitored by thermogravimetry under N<sub>2</sub> atmosphere in the presence of solid acid catalysts such as alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), crystalline silica-alumina (SA, molar ratio of Si/Al=0.19) and amorphous silica-alumina catalysts (ASA, molar ratio of Si/Al=4.9). Crystal structure and surface area of solid acid catalysts were measured by XRD and BET, respectively. The strength and distribution of acid sites of solid acid catalysts were estimated by NH<sub>3</sub>-TPD. It was observed that total acidity strength is in the order of ASA (1.77  $\mu$ mol NH<sub>3</sub>/g) > AS (1.42  $\mu$ mol NH<sub>3</sub>/g) >  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (1.06  $\mu$ mol NH<sub>3</sub>/g) >  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0.06  $\mu$ mol NH<sub>3</sub>/g). Thermal degradation behavior of LDPE with and without solid acid catalyst was monitored by TGA, where heating rates ( $\beta$ ) of 5, 10, and 20 °C/min were employed under an inert atmosphere, and their activation energies ( $E_a$ ), onset temperatures ( $T_{initial}$ ), decomposition temperatures ( $T_{decomp}$ ) were calculated and compared. The activation energy ( $E_a$ ) was evaluated using the Coats-Redfern method. Solid acid catalysts with stronger acidity and higher surface area showed a decrease in activation energy and onset temperature. Activation energy of LDPE over ASA catalyst is decreased to 97.3 kJ/mol from thermal decomposition of LDPE without catalyst of 117.2 kJ/mol under heating rate of 10 °C/min. The isothermal decomposition of LDPE was monitored at 300 °C for 3 h with a heating rate of 10 °C/min, where 13.1% and 24.2% wt. loss were observed over SA and ASA, respectively, while only 0.7% wt. loss was observed for LDPE without a solid acid catalyst.

## Graphical abstract

Single step decomposition of LDPE

Thermal degradation behavior of LDPE monitored by TGA, with different heating rates ( $\beta$ ) of 5, 10, 20 °C/min.



**Keywords** Solid acid catalysts · Thermal degradation · LDPE · TGA · Activation energy ( $E_a$ )

✉ Young Soo Kang  
yskang@kentech.ac.kr

<sup>1</sup> Korea Institute of Energy Technology (KENTECH),  
Environmental and Climate Technology, Naju 58330,  
Republic of Korea

## 1 Introduction

Waste plastics originally produced from petroleum resources (feedstocks) are not biodegradable and have been accumulated in the environment for several decades. Conventional ways such as incineration, landfilling, and composting with other materials are not effective for the disposal of waste plastic because they are critically harmful for the air, soil, water and ocean environments [1, 2]. At present, the most widely used plastics are high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), Polyethylene terephthalate (PET), and polyvinyl chloride (PVC). Waste generated from these polymers is valuable source of energy and it contains large number of hydrocarbons. One of the most important chemical recycling technologies is pyrolysis. The thermochemical breakdown of organic materials in the absence of oxygen is known as pyrolysis. When the pyrolysis is carried out in the absence of catalyst is known as thermal cracking, in this process, high temperatures (500 to 900 °C) are required, and it gives the high boiling point hydrocarbons as a products. On the other hand, in catalytic pyrolysis, the reaction temperature is lowered with the use of an appropriate catalyst to speed up the cracking reaction [3]. In fact, there are many reports on the catalytic cracking of polymers as an alternative way of waste plastic recycling and conversion into valuable hydrocarbons [3–5]. The catalytic effect on the polymer decomposition can be evaluated by various methods, but thermogravimetric analysis is one of the most effective ways for the quantitative and qualitative analysis because it shows basic information for the thermal decomposition behavior under various reaction conditions [6, 7]. It can be a potential method for screening catalysts based on the degradation efficiency depending on the degradation temperature, and it also allows the kinetic data by the polymer structure, composition, and operating conditions during thermal degradation [8]. Conventionally thermogravimetry has been studied to estimate the activation energy for the catalytic degradation of polymer where the presence of a catalyst led to a decrease in the activation energy [9].

Main purpose of this study is to study the effect of acidity of solid acid catalysts during non-oxidative thermal decomposition of LDPE and its effect on activation energies ( $E_a$ ). Non-oxidative thermal decomposition of LDPE was performed over solid acid catalysts such as two alumina ( $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\gamma$ - $\text{Al}_2\text{O}_3$ ), amorphous silica-alumina (ASA) and silica-alumina (SA) with different Si/Al mole ratios. Crystal structure and surface area of solid acid catalysts were measured by XRD and BET, respectively. The strength and distribution of acid sites were estimated by  $\text{NH}_3$ -TPD. Park *et al.* reported kinetic analysis using

the various analytical methods showed the tremendous variations depending upon the mathematical approach taken in the analysis [9]. Thermal degradation behavior of LDPE with and without solid acid catalysts was monitored by TGA and their apparent activation energies ( $E_a$ ) were calculated using the Coats-Redfern method and compared [10]. The relationship between the acidity/surface area of solid acid catalysts and the thermal decomposition behaviors such as onset temperature, decomposition temperature were investigated based on  $\text{NH}_3$ -TPD, BET, and TGA. From this study, the results indicate that stronger acidity and higher surface area of solid acid catalyst led to higher thermal degradation efficiency of LDPE.

## 2 Experimental

### 2.1 Materials

LDPE polymer used in this work is a commercial one with 5 mm nominal granule size supplied by Sigma-Aldrich Co. Before the experiments, the LDPE was crushed and sieved to a particle size of less than 1.0 mm. The  $\gamma$ - $\text{Al}_2\text{O}_3$  supplied by Alfa Aesar, a Johnson Matthey Co. (aluminum oxide, gamma-phase), crystalline silica-alumina (SA) with Si/Al molar ratio of 0.19 supplied by Sasol Co. (SIRAL 10) and amorphous silica-alumina (ASA) with Si/Al molar ratio of 4.9 supplied by Sigma-Aldrich Co. All the acid catalysts were calcined at 400 °C for 4 h in air prior to each experiment.

### 2.2 Catalyst characterization

The phase of the materials is investigated through the powder X-ray diffraction (XRD) analysis using Miniflex 600 Rigaku diffractometer equipped with Cu  $K\alpha$  source ( $\lambda = 1.5418 \text{ \AA}$ ), scan in the 10–80° range at a rate of 2°/min operating at 30 kV and 40 mA.

The acidity of the catalysts was measured by temperature programmed desorption of ammonia ( $\text{NH}_3$ -TPD) using Autochem II 2920 chemisorption analyzer (Micromeritics Instruments, USA). A 0.1 g of catalyst was placed in an adsorption vessel and heated to 450 °C in He flow for 1 h at a rate of 10 °C/min. Later it was cooled down to 100 °C under the He flow. At this temperature, 15%  $\text{NH}_3$  in  $\text{N}_2$  was passed through the sample at a flow rate of 30 ml/min for 1 h. Then,  $\text{NH}_3$  gas was shifted to He and cooled to room temperature. TPD was run from room temperature to 600 °C at a heating rate of 10 °C/min with He flow at 30 ml/min. The amount of ammonia desorbed in the reactor was monitored by a thermal conductivity detector (TCD). The total acidity of the catalyst was obtained by integrating the area

under the desorption curve while its strength is related to the temperature of ammonia desorption.

BET surface of the ASA and  $\alpha$ - $\text{Al}_2\text{O}_3$  catalysts were measured using liquid nitrogen by an ASAP2420 Micromeritics Adsorption Analyzer (Micromeritics Instruments, USA). Catalysts were degassed at 250 °C for 2 h prior to the measurements to remove the adsorbed moisture from the catalyst's surface and pores. The BET area was calculated from the Brauer-Emmett-Teller (BET) equations by the instrument software. The surface area of SA (Siral 10) is well reported by Sasol Co. and the surface area for  $\gamma$ - $\text{Al}_2\text{O}_3$  was reported elsewhere [11].

Si/Al molar ratio of ASA was determined by X-ray fluorescence spectroscopy (XRF) analysis.

The homogeneity of LDPE and ASA catalyst mixture were examined by scanning electron microscopy (SEM, Helios G5 UX, Thermo Fisher Scientific, USA) at an acceleration voltage of 15 kV and a working distance of 4.0 mm and energy dispersive X-ray spectrometry (EDS) mapping.

### 2.3 Thermogravimetric analysis

A TA instruments Q50 DSC-TGA thermal analyzer was used to conduct TGA experiments to determine the degradation profile of LDPE with and without a catalyst. To create an inert atmosphere, nitrogen (99.99% minimum purity) is used with a flow rate of 30 ml/min. The sample temperature is measured with a thermocouple placed directly in the sample holder. Intimate contact between LDPE and catalyst is requisite for the LDPE decomposition using solid acid catalysts. Five samples were prepared to analyze TGA, the first one pure LDPE and the others are LDPE and catalysts mixture with 1 to 9 (w/w) ratio. To get homogeneous mixture of LDPE and catalyst, both LDPE and catalyst were used in powdered for, first 4 mg of LDPE and 36 mg of catalysts were mixed in an agate mortar and from this homogeneous mixture took 10–15 mg of sample for TGA analysis [12–14]. In each experiment, a 10–15 mg sample was placed in a platinum pan and was decomposed from 40 °C to 600 °C at heating rates of 5, 10, and 20 °C/min.

## 3 Results and discussion

### 3.1 Catalyst characterization

The catalysts were thoroughly characterized to gain insight into the relationship between the catalyst surface properties (acidity and surface area) and the decomposition behavior of LDPE.

Figure 1 displays the X-ray diffractograms for all the catalysts under investigation. ASA catalyst exhibited a typical

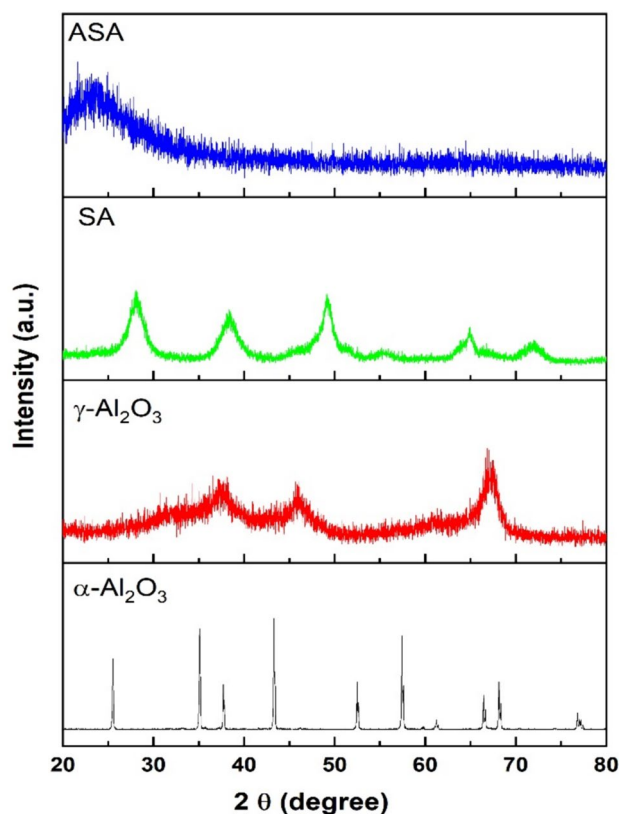


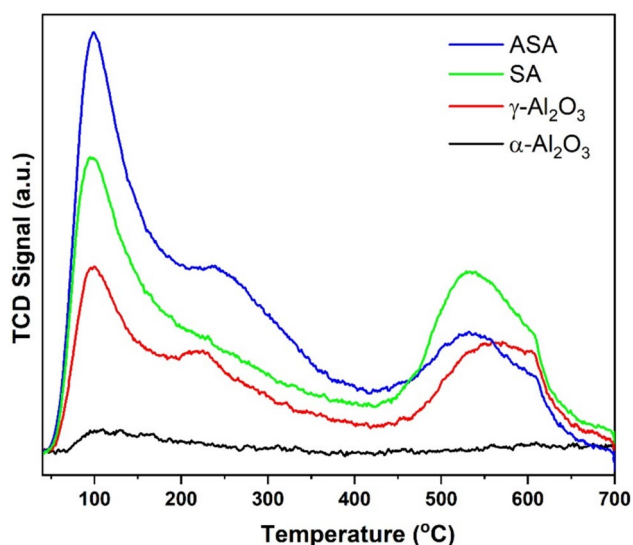
Fig. 1 XRD patterns for  $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\gamma$ - $\text{Al}_2\text{O}_3$ , SA and ASA catalysts

halo at  $2\theta$  of 23–24°, which is an indicative peak for amorphous silica-alumina, results from the dispersion of the angles and bond distances between the basic structural units (silicates and aluminates) which destroy the structure periodicity and produce a non-crystalline material [15]. For SA (SIRAL 10, with 90% of  $\text{Al}_2\text{O}_3$  content), the peaks at  $2\theta$  of 39.5°, 46°, and 67.4° are clearly observed, which are attributed to  $\gamma$ - $\text{Al}_2\text{O}_3$  substrate [16–18], whereas an amorphous hump at  $2\theta$  of 23° belongs to amorphous silica [18]. XRD patterns of  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\gamma$ - $\text{Al}_2\text{O}_3$ , were identified as typical  $\alpha$  and  $\gamma$  phases, respectively. For  $\alpha$ - $\text{Al}_2\text{O}_3$ , peaks appear at  $2\theta$  of 25.6°, 35.1°, 37.7°, 43.3°, 46.1°, 52.5°, 57.4°, 61.27°, 66.5° and 68.2° (JCPDS file No. 88–0826) [19]. Atsushi Satsuma *et al* [20]. Reported XRD patterns of  $\text{Al}_2\text{O}_3$  are analogous to our results (Fig. 1).  $\gamma$ - $\text{Al}_2\text{O}_3$  exhibits peak at  $2\theta$  of 37.2°, 45.6°, and 66.9° is the characteristics peak for the gamma phase of  $\text{Al}_2\text{O}_3$  [17].

$\text{NH}_3$ -TPD was used to characterize the acidic properties of the catalysts, it allows us to estimate the total acidity and acidic strength distribution of the catalyst. Table 1 displays the TPD results of catalysts, and Fig. 2 displays their profiles. Total acidic strength and its distributions into weak, medium, and strong are determined by measurement of the total amount of  $\text{NH}_3$  chemisorbed at different temperatures. Peaks assigned at lower and higher

**Table 1** Surface area and acidity of solid acid catalysts

Solid acid catalysts	Si/Al <sup>a</sup> (molar ratio)	BET (m <sup>2</sup> /g) <sup>b</sup>	Acid strength distribution (μmol NH <sub>3</sub> /g) <sup>c</sup>			
			Weak <sup>d</sup> (μmol NH <sub>3</sub> /g)	Medium <sup>e</sup> (μmol NH <sub>3</sub> /g)	Strong <sup>f</sup> (μmol NH <sub>3</sub> /g)	Total acidity <sup>g</sup> (μmol NH <sub>3</sub> /g)
α-Al <sub>2</sub> O <sub>3</sub>	–	8	0.06	–	–	0.06
γ-Al <sub>2</sub> O <sub>3</sub>	–	250	0.38	0.35	0.31	1.06
SA	0.19	370	0.39	0.61	0.41	1.42
ASA	4.9	489	0.54	0.85	0.3	1.77

<sup>a</sup>Observed from XRF<sup>b</sup>Calculated from the N<sub>2</sub> adsorption desorption isotherms<sup>c</sup>Calculated from the NH<sub>3</sub>-TPD measurements<sup>d</sup>Temperature range between 110 °C and 230 °C<sup>e</sup>Temperature range between 230 °C and 400 °C<sup>f</sup>Temperature range between 400 °C and 600 °C<sup>g</sup>Summations of (d), (e) and (f)**Fig. 2** NH<sub>3</sub>-TPD of α-Al<sub>2</sub>O<sub>3</sub>, γ-Al<sub>2</sub>O<sub>3</sub>, SA and ASA catalysts

temperatures could be attributed to NH<sub>3</sub> desorbed from weak and strong acid sites. Generally peak observed in the range of 100–270 °C and 270–400 °C is due to weak and medium acidic strength, respectively and the peak at 400–600 °C is due to the presence of strong acidic sites [21]. SA and ASA catalysts have a larger number of acidic sites than both alumina (α-Al<sub>2</sub>O<sub>3</sub>, γ-Al<sub>2</sub>O<sub>3</sub>) catalysts. As shown in Fig. 2, there are no desorption peaks observed for α-Al<sub>2</sub>O<sub>3</sub>, indicating that α-Al<sub>2</sub>O<sub>3</sub> may not possess an acidic site. For the SA catalyst, broad desorption peaks were observed in the temperature range of 400–600 °C showing the presence of strong acidic sites which is higher than that of γ-Al<sub>2</sub>O<sub>3</sub> and ASA catalyst. From Table 1, the strong acidic strength for SA catalyst is 0.41 μmol/g, which is slightly higher than that of γ-Al<sub>2</sub>O<sub>3</sub> (0.31 μmol/g) and

ASA (0.3 μmol/g) catalyst. The total acidity of the selected catalyst was in the order of (ASA) > (SA) > (α-Al<sub>2</sub>O<sub>3</sub>). The total acidic strength of γ-Al<sub>2</sub>O<sub>3</sub>, SA, and ASA are 1.06 μmol/g, 1.42 μmol/g, and 1.77 μmol/g, respectively. Among all catalysts, ASA catalyst has the highest total acidic strength. The weak acidic strength of 0.38 μmol/g and medium of 0.35 μmol/g were found for γ-Al<sub>2</sub>O<sub>3</sub> catalyst. For SA catalyst weak and medium acidic strength of 0.39 and 0.61 μmol/g were found. Whereas the weak and medium acidic strength of ASA catalyst is 0.54 and 0.84 μmol/g, respectively. The difference obtained in the NH<sub>3</sub>-TPD profile is explained by different Si/Al ratio. As the Si/Al ratio increase indicates a decrease in the number of Al<sup>+</sup> cation sites in the adjustment position, which provides a strong acidic site (Brønsted acidic site) due to their isolation [13].

SA and ASA showed large surface areas (370 and 489 m<sup>2</sup>/g, respectively) followed by γ-Al<sub>2</sub>O<sub>3</sub> (250 m<sup>2</sup>/g), on the other hand, α-Al<sub>2</sub>O<sub>3</sub> had the smallest surface area (8 m<sup>2</sup>/g). The Si/Al ratio was determined by XRF analysis and summarized in Table 1. For the ASA catalyst, the Si/Al molar ratio is 4.9, whereas for the SA catalyst, it is 0.19. Aluminum (Al) content in solid acid catalysts determines the acidity and it influences the catalytic performance of materials [8, 13, 21].

To check the homogeneity of LDPE and ASA catalyst mixture, we performed SEM in combination with EDS mapping. EDS elemental distribution maps of LDPE and ASA catalyst mixture displayed in Fig. 3. We can map the distribution of oxygen (O), silicon (Si) and aluminum (Al) which are the basic components of ASA catalyst, along with these elements we clearly observed carbon (C) on a catalyst surface. These maps reveal homogeneous distribution of carbon (LDPE) across the ASA catalyst.



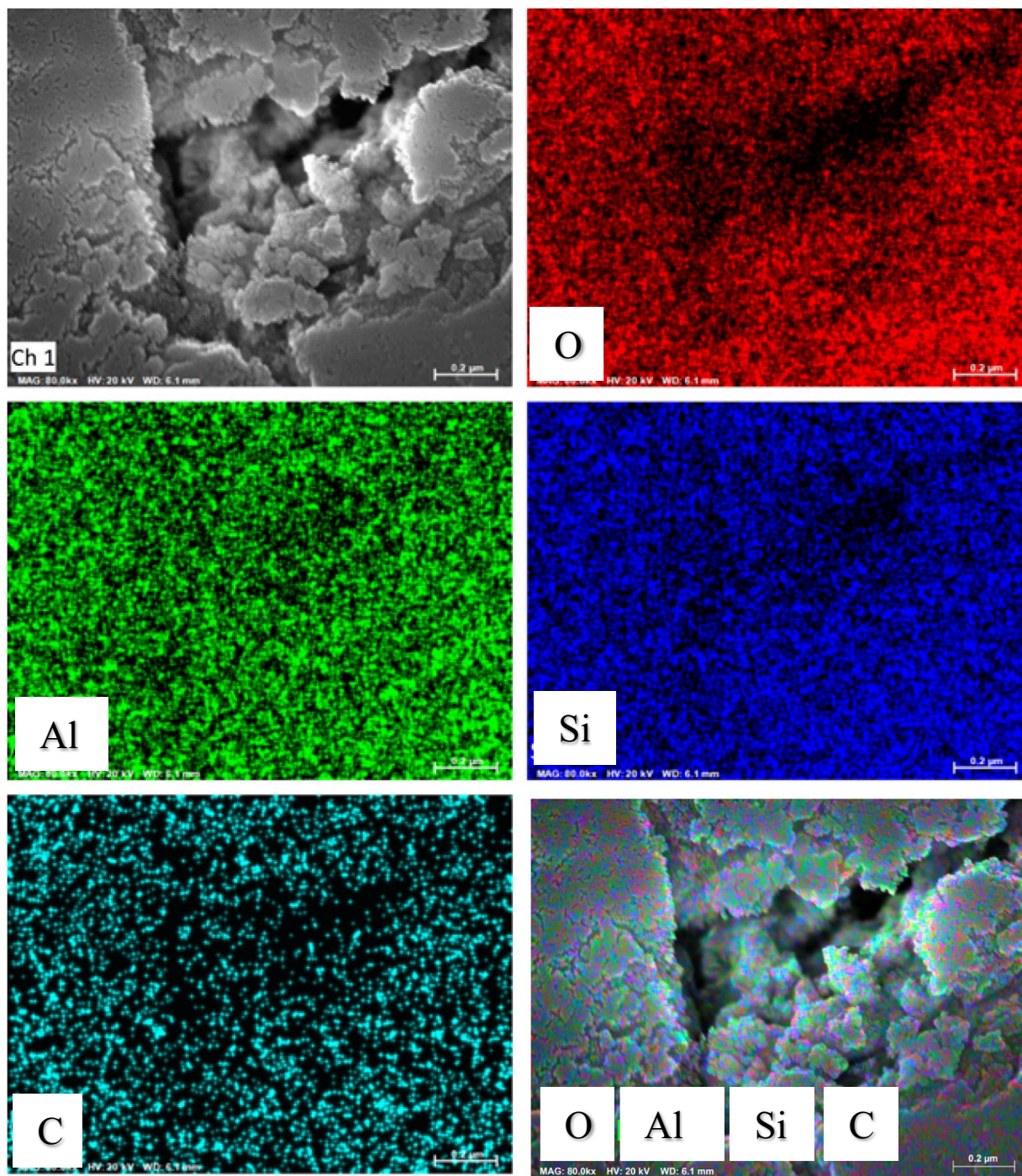


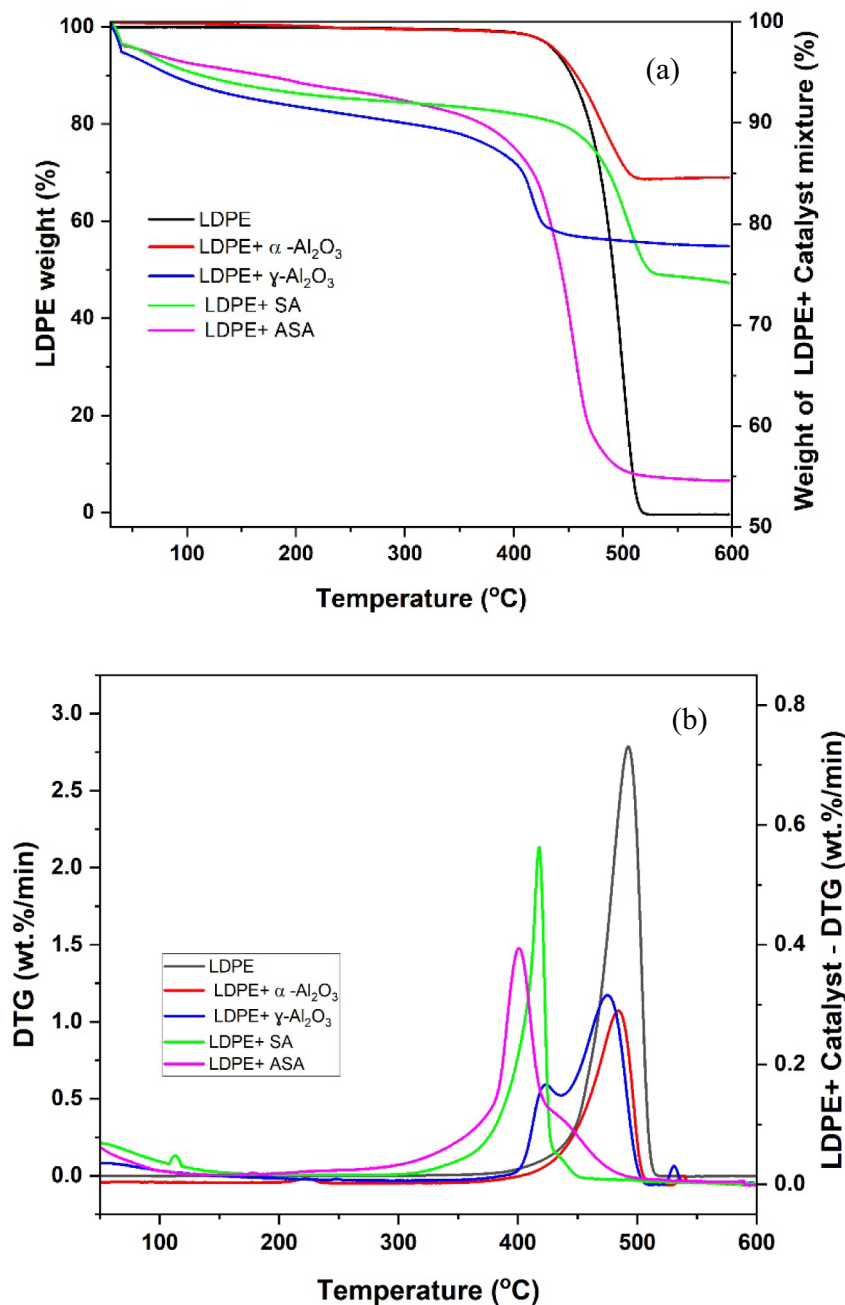
Fig. 3 SEM, SEM-EDS mapping images spectrum of LDPE+ASA catalyst

### 3.2 Kinetic parameter calculation by TGA

To understand the decomposition behavior of LDPE, thermogravimetric analysis (TGA) is a valuable technique to get important information on the thermal stability and degradation steps of LDPE. TGA can also give useful information

regarding on the energy required for plastic degradation in the presence or absence of catalyst. It is a useful tool for the preliminary screening of potential candidates of catalysts [10–14]. Figure 4 and Table 2 show the results obtained for the thermal and catalytic decomposition of LDPE under  $N_2$  atmosphere at a heating rate of  $10\text{ }^\circ\text{C}$  using  $\alpha\text{-Al}_2\text{O}_3$ ,

**Fig. 4** TG degradation curves for LDPE and LDPE and their mixture with catalysts with 1/9 ratio. **a** TGA for LDPE,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SA and ASA and **b** DTG their 1st derivatives with heating rate 10 °C/min



$\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SA, and ASA catalysts and the graphs were plotted in accordance with previously published report [22].

In the TGA curve, the initial temperature of the degradation ( $T_{\text{initial}}$ ) is the temperature at 10% of conversion of LDPE ( $T_{10\%}$ ) and final temperature ( $T_{\text{final}}$ ) is for complete degradation of LDPE are shown in Table 2. LDPE thermal degradation without catalyst was initiated at about 457 °C. But thermal degradation of LDPE with catalyst initiated the mass loss at lower temperatures depending upon the

kinds of catalysts [23]. There was a clear shift of  $T_{\text{initial}}$  for all the catalysts except  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. It was observed that  $T_{\text{initial}}$  shifted slightly to higher temperature with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (479 °C). This can be caused because,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> having no acidic site and extremely small surface area, hence providing little space for the LDPE cracking reaction. The same trend has been reported by Nisar et al. [24].  $T_{\text{initial}}$  of LDPE using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, SA, and ASA catalysts was 300 °C, 371 °C and 438 °C, respectively.

**Table 2** TGA results obtained during the non-oxidative decomposition of LDPE over solid acid catalysts under heating rate of 10 °C/min

Catalysts	T <sub>initial</sub> <sup>a</sup> (°C)	T <sub>final</sub> (°C)	T <sub>decomposition</sub> (°C) <sup>b</sup>		Mass loss <sup>c</sup> (wt%)	Residual mass <sup>d</sup> (wt%)	Isotherm mass loss (wt.) <sup>e</sup>
			1st	2 <sup>nd</sup>			
LDPE	457	520	–	501	99.7	0.3	0.7
α-Al <sub>2</sub> O <sub>3</sub>	479	514	–	504	15.4	84.6	n.d
γ-Al <sub>2</sub> O <sub>3</sub>	300	432	–	479	24.9	75.1	n.d
SA <sup>e</sup>	371	492	–	455	45.4	54.6	13.1
ASA <sup>f</sup>	438	526	–	416	21.4	78.6	24.2

<sup>a</sup>Observed from TGA, T<sub>initial</sub> = T<sub>(10%)</sub>

<sup>b</sup>The peak of the 1st derivative indicates the point of the greatest rate of change on the wt. loss curve

<sup>c</sup>Up to the temperature of 600 °C

<sup>d</sup>In the final temperature of 600 °C equivalent to the summation of weights for the catalyst

<sup>e</sup>Silica-alumina

<sup>f</sup>Amorphous silica-alumina

<sup>g</sup>Isothermal decomposition of LDPE at 300 °C for 3 h

The isothermal decomposition of LDPE was also studied. Isothermal means heating the sample at a specified temperature for a selected time. The isothermal decomposition of LDPE monitored at 300 °C for 3 h with a heating rate of 10 °C/min, where 13.1% and 24.2% wt. loss were observed over SA and ASA, respectively, while only 0.7% wt. loss was observed for LDPE without a solid acid catalyst (Figure S3).

Weight loss profiles for all of catalysts show a similar pattern, with a single degradation step, indicating that LDPE degradation occurs in one stage. Even at the different heating rates, (Figs. S2 and S3) LDPE degradation occurs in a single stage, but the temperature range of the decomposition process is influenced by the heating rate. An increase in the heating rate leads to a shift of TGA curves towards higher temperatures as shown in Table 3. TGA and DTG curves at different heating rates (5, 10, and 20 °C) are shown in Figs. 3, S2, and S3, respectively. The decomposition temperature (T<sub>decomp</sub>) and activation energy (E<sub>a</sub>) of LDPE under varying heating rates (β) during its non-oxidative degradation over solid acid catalysts are presented in Table 3. Activation energy is the minimum amount of energy required for LDPE degradation reaction to

occur. Sinfonia et al. well reported the kinetic parameters such as activation energy, frequency factor and reaction order, were measured under dynamic conditions using Flynn–Wall–Ozawa, Van Krevelen, Horowitz–Metzger, Coats–Redfern, Madhusudan and Vyazovkin methods [23]. In our study, the activation energy (E<sub>a</sub>) was evaluated using the Coats–Redfern method [10]. Abbas *et al.* described well on the detailed calculation and method in their report [14]. Coats–Redfern method was used to calculate activation energy of LDPE decomposition based on the following equation for first order reaction (1).

$$\ln \left[ \frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E_a} \right] - \frac{E_a}{RT} \quad (1)$$

where α is conversion ratio of LDPE, and is given by:

$$\alpha = \frac{m_0 - m}{m_0 - m_f}$$

m<sub>0</sub> is the initial sample weight, m is the sample weight at time t, m<sub>f</sub> is the final sample A is the pre-exponential factor and R is gas constant. Equation 1 is used to plot the [-ln(1-α)/T<sub>2</sub>] versus 1000/T graph, the slope of a resultant

**Table 3** Decomposition temperature (T<sub>decomp</sub>) and activation energy (E<sub>a</sub>) obtained during the non-oxidative decomposition of LDPE over solid acid catalysts under different heating rate (β)

Catalysts	β = 5 °C/min		β = 10 °C/min		β = 20 °C/min	
	T <sub>decomp</sub> <sup>a</sup> (°C)	E <sub>a</sub> (KJ/mol)	T <sub>decomp</sub> <sup>a</sup> (°C)	E <sub>a</sub> (KJ/mol)	T <sub>decomp</sub> <sup>a</sup> (°C)	E <sub>a</sub> (KJ/mol)
LDPE	492	112	501	117.2	527	126.3
α-Al <sub>2</sub> O <sub>3</sub>	485	109.2	504	115.3	505	121.1
γ-Al <sub>2</sub> O <sub>3</sub>	475	108.1	479	113	513	119.3
SA	417	105.8	455	101.2	460	106.5
ASA	400	93.7	416	97.3	440	98.1

<sup>a</sup>The peak of the 1st derivative indicates the point of the greatest rate of change on the wt. loss curve obtained from DTG curve, β is heating rate

<sup>b</sup>Average activation energy (E<sub>a</sub>) calculated by the Coats–Redfern method [10]



straight line from the plotted data, used to estimate the activation energy ( $E_a$ ).

Table 3 demonstrates that there is a decrease in activation energy when using the solid acid catalyst with a high surface area. The activation energy ( $E_a$ ) for non-catalytic degradation of LDPE was observed at 117.2 kJ/mole, which was decreased to 101.2 kJ/mole when the SA catalyst was used and 97.3 kJ/mole with ASA catalyst under heating rate of 10 °C/min. The  $E_a$  for LDPE degradation without catalysis was found to be 112.0 kJ/mole; this reduced to 105.8 kJ/mole when the SA catalyst was employed, and to 97.3 kJ/mole when the ASA catalyst was used at 5 °C/min heating rate. The  $E_a$  for the non-catalytic degradation of LDPE was measured at 126.3 kJ/mole; this dropped to 106.5 kJ/mole when using the SA catalyst, and to 98.1 kJ/mole when using the ASA catalyst at a 20 °C/min heating rate. Park et al. [9] reported 123 kJ/mol of  $E_a$  at 10 °C/min for the thermal decomposition of the HDPE by CR method. The  $E_a$  values in Table 3 indicated that the presence of solid acid catalysts decrease the activation energy of LDPE decomposition compared with thermal decomposition.

Additionally, from Fig. 3(b) and Table 3, it is clearly shown that the increased heating rate resulted in an increased  $T_{\text{decomp}}$  for LDPE because of the shorter time to release the heat with increasing heating rate, leading to slower degradation rate and higher degradation temperature in both thermal and catalytic degradation. Maximum weight loss temperature of LDPE was 501 °C, decreasing to 479 °C for  $\gamma$ - $\text{Al}_2\text{O}_3$ , 455 °C for SA, and 416 °C for ASA catalysts. It is less by 22 °C, 46 °C, and 85 °C compared with pure LDPE maximum degradation temperature. Therefore, it is clearly observed, the effect of acidity and surface area of the catalysts play a critical role in the degradation of LDPE [25]. TGA results obtained during the non-oxidative decomposition of LDPE over solid acid catalysts under heating rate of 5 °C/min and 20 °C/min follow the same trend (Table S1 and Table S2). It indicates that during thermo-catalytic decomposition, the LDPE melts, and spreads around the active outer surface site of the solid acid catalysts for the efficient degradation.

## 4 Conclusion

Catalytic thermal decomposition of low-density polyethylene was studied by thermogravimetry under  $\text{N}_2$  atmosphere with 3 different heating rates ( $\beta = 5, 10, 20$  °C) over 4 different solid acid catalysts ( $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\gamma$ - $\text{Al}_2\text{O}_3$ SA and ASA) with different surface area (8, 520, 370, 489  $\text{m}^2/\text{g}$ ) and acidity (0.06, 1.06, 1.42, 1.77  $\mu\text{mol NH}_3/\text{g}$ ). Effect of acidity and surface area of the solid acid catalyst were studied. TGA is a convenient and useful tool for the investigation of thermal

and catalytic degradation of polymer. The activation energy, onset temperature and decomposition temperature (point of the greatest rate of change on the weight loss curve) were calculated and compared. Solid acid catalyst with stronger acidity and higher surface area showed a decrease in activation energy, onset temperature and decomposition temperature. As the thermal decomposition reaction of polymer is endothermic, the input heat energy will be required for the dissociation of C–C bond in the polymer. And the direct relationship between the dissociation energy of C–C bond and the decomposition temperature can be found. During thermal decomposition of polymer, the single step process can be used to describe the apparent kinetics of degradation in the narrow range of heating rates and operating conditions. It can be assumed that volatilization products will be formed through a large number of independent parallel first-order reactions with different activation energies. The temperature dependence of the rate constant is described by the Arrhenius equation and TGA curves shifts to higher temperature as the heating rate increased from 5 to 20 °C/min for all catalysts. This is due to the shorter time requirements for the sample to reach a given temperature at increased heating rate. The addition of a catalyst substantially decreases the degradation temperature of LDPE, regardless of the heating rate in the thermogravimetric degradation test.

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## Declaration

**Conflict of interest** The authors declare that they have no conflict of interest.

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