ABSTRACT: Nowadays, the increase in plastic waste is causing serious environmental problems. Catalytic cracking has been considered a promising candidate to solve these problems. Catalytic cracking has emerged as an attractive process that can produce valuable products from plastic wastes. Solid acid catalysts such as zeolites decompose the plastic waste at a lower temperature. The lower decomposition temperature may be desirable for practical use. Herein, we synthesized both Zr- and Al-incorporated Beta zeolite using amorphous ZrO$_2$-$\text{SiO}_2$. The optimized Zr content in the dry gel allowed the enhancement of Lewis acidity without a significant loss of Brønsted acidity. The enhancement of Lewis acidity was mainly due to Zr species incorporated into the zeolite framework. Thanks to the enhanced Lewis acidity without any significant loss of Brønsted acidity, higher polymer decomposition efficiency was achieved than a conventional Beta zeolite.

1. INTRODUCTION

Plastics are used in our daily lives in a number of applications. Thus, the production, consumption, and waste generation rate of plastic have increased considerably.$^{1,2}$ These plastic wastes have generated serious environmental problems. Therefore, plastic waste recycling has been a focus of many researchers in the past few decades. The current plastic recycling methods can be divided into three main categories.$^{3–9}$ Material recycling is a recycling method that utilizes the structure of plastics. However, it is not widely used because it often degrades its physical and chemical effects.$^{10}$ Thermal recycling is the most widely used method, but it causes serious damage to the global environment. Recently, chemical recycling (CR) has been considered as an attractive candidate to solve the above drawbacks.$^{11–15}$

CR can allow wasted plastics to be processed into valuable products (e.g., monomers, petrochemical feedstock, and fuel fractions)$^{1,16–29}$ Thermal cracking, which is a CR method, requires very high temperatures, leading to high energy consumption. Additionally, thermal cracking gives products with a wide product distribution. Meanwhile, catalytic cracking has appeared as an alternative option. Unlike thermal cracking, catalytic cracking has been expected to achieve both reductions in energy consumption and control of product distribution through precise catalyst design.$^{30,31}$ Recently, there has been much research on the catalytic cracking of polymers using zeolites, which represent solid acid catalysts.$^{32–41}$

In the catalytic cracking of polymers, the catalytic performance highly depends on the zeolite structure.$^{1}$ Due to the large molecular size of the polymer compared with the zeolitic micropore size, the initial reaction of polymer degradation occurs at the external surface or zeolitic micropore mouths.$^{42}$ For this reason, zeolites with a large external surface area exhibit high activity. As the decomposition reaction proceeds, the molecular size of the reactants is reduced, but diffusion into the micropores of the zeolite is often restricted. Because of the above, it is known that BEA-type zeolites with a high external surface area and large micropores$^{43}$ exhibit very high activity on catalytic polymer cracking.$^{1}$ However, because the control of morphology is reaching its limits, new approaches are needed to improve the catalytic activity further.

Zeolites are crystalline microporous aluminosilicates with tetrahedrally connected framework structures.$^{44}$ Tetrahedral TO$_4$ units (T = Si, Al, etc.) constitute the three-dimensional crystalline porous frameworks of zeolites sharing oxygen atoms. The isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ induces the negative charge of zeolite frameworks, where cations are located to balance the overall charge.$^{44,45}$ Specific functions of zeolites often originate from these cations;$^{46}$ proton-exchanged zeolites have both strong Brønsted/Lewis acid sites.$^{47}$ This Lewis acid site is mainly generated by structural defects such as
silanol groups and extra-framework hexacoordinated aluminum.\textsuperscript{48–50} It is known that both the Brønsted and Lewis acidities are important in polymer degradation.\textsuperscript{51} BEA-type (Beta) zeolite is suitable for the catalytic decomposition of polymers because they have many Lewis acid sites derived from structural defects as well as Brønsted acid sites. We have previously improved the catalytic activity of Beta in the degradation of polymers by intentionally increasing the Lewis acid sites derived from structural defects.\textsuperscript{52}

However, there is a limit to the number of structural defects introduced. Therefore, another approach must be developed to improve the Lewis acidity of Beta zeolites to further improve activity toward low density polyethylene (LDPE) cracking. In general, the Beta zeolites with enhanced Lewis acidity can be synthesized by introducing tetravalent heteroatoms (Zr, Ce, Sn, etc.) into their framework.\textsuperscript{53–55} These heteroatom-incorporated Beta zeolites are often synthesized using dealuminated Beta zeolites.\textsuperscript{55} However, the Bronsted acid sites generated by Al disappear in this method during a dealumination process. In this study, we aimed to improve the Lewis acidity of Beta zeolites by introducing Zr into the framework without a dealumination treatment while maintaining the Al sites showing Bronsted acidity. Moreover, the prepared samples were applied in a polymer decomposition reaction analyzed by thermogravimetry.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis. According to our previous reports,\textsuperscript{56,57} amorphous ZrO\textsubscript{2}–SiO\textsubscript{2} was prepared as a precursor gel using zirconium butoxide and tetramethyl orthosilicate. Zirconium butoxide and tetramethyl orthosilicate were added into tetrahydrofuran solution. The molar ratio was Si/Zr = x (x = 10, 50). Deionized water was dropped into the above mixture. Then, milky solid materials of ZrO\textsubscript{2}–SiO\textsubscript{2} were formed through hydrolysis reactions. The milky solid materials of ZrO\textsubscript{2}–SiO\textsubscript{2} were separated from the suspension by centrifugation and calcined at 673 K for 5 h. The obtained powder was labeled as ZrO\textsubscript{2}–SiO\textsubscript{2}(x).

We synthesized zeolites by a dry gel conversion method referring to our previous report.\textsuperscript{52} Here, we used aluminum sulfate hexadecahydrate, Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}·16H\textsubscript{2}O, and 35 wt % tetraethylammonium hydroxide (TEAOH) aqueous solution. The precursor solutions were prepared at the mass ratios of 1 ZrO\textsubscript{2}–SiO\textsubscript{2}(x)/0.57 Al\textsubscript{2}O\textsubscript{3}/1.2 TEAOH/0.2 NaOH/11.2 H\textsubscript{2}O. The precursor solutions were stirred at room temperature for 2 h, and then evaporation was performed to obtain a dry gel. The dry gel was crystallized under steam in an autoclave at 453 K for 72 h. The resultant powder was collected by centrifugation and washed with deionized water. This washing process was repeated three times, and the obtained powder was dried at 363 K. In order to remove the organic structure-directing agent (OSDA), calcination under air was performed at 823 K for 5 h. We used 1 mol L\textsuperscript{−1} aqueous ammonium chloride solution to change the cation from Na\textsuperscript{+} to NH\textsubscript{4}\textsuperscript{+}. Then, calcination was performed at 823 K for 5 h to obtain a H\textsuperscript{+}-type sample. The obtained sample was named Beta-SZ(x), where x represents the molar ratio of Si/Zr, as shown above. As a comparison, conventional Beta zeolite was prepared through a similar procedure.

2.2. Characterization. The crystal structures of all products were determined by X-ray diffraction (XRD) patterns using a PANalytical X’Pert-MPD diffractometer with Cu Kα radiation. The energy-dispersive X-ray spectroscopy (EDX) for the determination of Zr and Al content was carried out using JEOL JCM-7000. N\textsubscript{2} adsorption measurements at 77 K were conducted using BELSORP-Max (MicrotracBel). The particle size and external surfaces of samples were observed by transmission electron microscopy (TEM). Diffuse reflectance ultraviolet–visible (UV–vis) spectra of the samples were obtained on a JASCO V-770 spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was performed on a JPS-9000MX spectrometer (JEOL) with Mg Kα source radiation (10 kV, 10 mA) as the energy source. The \textsuperscript{27}Al MAS NMR spectrum was measured to determine the state of Al. IR spectra were recorded with an MCT detector in the 4000–400 cm\textsuperscript{−1} range. Before the IR measurements, pyridine was adsorbed and evacuated at 423 K for 15 min.
2.3. Catalytic Cracking of LDPE. The catalytic activity of the obtained samples for cracking of LDPE was investigated by using thermogravimetric analysis (TGA) according to our previous work. An alumina pan was applied for TGA. The mass ratio of catalyst/LDPE mixtures was fixed at 20 wt %. The mixtures were heated to 873 K with a heating rate of 5 K min⁻¹ under N₂ atmosphere.

3. RESULTS AND DISCUSSION

To analyze the crystal materials in catalysts, XRD patterns were investigated. The XRD patterns of the Beta-SZ samples with different Si/Zr ratios showed peaks similar to those of the reference BEA-type zeolite (Beta), as shown in Figure 1a. Beta zeolite consists of a highly faulted intergrowth of three polymorphs: A, B, and C. All samples showed a broad peak centered at around 8°, which is caused by overlapped peaks from the three polymorphs. Meanwhile, all samples showed a sharp peak centered at around 23° in their XRD patterns. Interestingly, this sharp peak, which is derived from the (302) plane of Beta zeolite, shifted to a lower angle by adding Zr (Figure 1b), implying the d-spacing of the (302) plane expanded by introducing Zr. The deformation of the zeolite structure was caused by the incorporation of Zr into the framework due to the large ion size of Zr compared with Si. No other peaks, such as those from crystalline impurities such as zirconium oxide, were detected within the limits of XRD.

EDX analyses were conducted to confirm the presence of Zr and Al in the samples and to obtain the Si/Zr ratio and Si/Al ratio in the catalysts. Compared to Beta, Beta-SZ was found to have a high content of both Al and Zr, as shown in Table 1.

Table 1. Physical and Chemical Properties of Beta and Beta-SZ

| catalysts  | Si/Al | Si/Zr | (Si + Zr)/Al | S_{ext} [m² g⁻¹] |
|------------|-------|-------|-------------|-----------------|
| Beta       | 12.0  | 59    |             | 285             |
| Beta-SZ(50)| 9.41  | 8.74  | 10.50       | 219             |
| Beta-SZ(10)| 9.11  | 7.24  | 10.53       | 134             |

The content of Zr in the products was higher than that in the starting materials. This is because of the difference of reactivity on hydrolysis between zirconium butoxide and tetramethyl orthosilicate. The reactivity of zirconium butoxide is much higher on hydrolysis than that of tetramethyl orthosilicate. The reactivity of zirconium butoxide is much higher on hydrolysis than that of tetramethyl orthosilicate. Therefore, all zirconium butoxide was converted first, while unreacted tetramethyl orthosilicate remained in the solvent. Thus, the precursor amorphous ZrO₂–SiO₂ had higher Zr content than the starting materials, leading to the formation of the final products with higher Zr content. The crystal shapes and particle sizes of Beta and Beta-SZ were investigated using TEM observations. Their TEM images showed similar aggregated nanoparticles with polycrystalline, as shown in Figure 2.

To estimate the external surface areas (S_{ext}) of samples, we applied the t-plot using N₂ adsorption isotherms of these samples. All samples have high S_{ext} (over 100 m²/g), as shown in Table 1. The introduction of Zr caused a decrease in the external surface areas per unit mass. This is due to the incorporation of Zr, which has a larger atomic weight than Si, into the zeolite framework. As for Beta-SZ(10), however, the decrease in S_{ext} is so drastic that it cannot be explained by the difference in atomic weight, so there is a possibility that bulky byproducts were formed.

The clear chemical state of Zr species in zeolites was characterized using UV–vis and XPS spectroscopies. A strong absorbance appeared at 230 nm for a reference ZrO₂. The strong absorbance is ascribed to the Zr–O–Zr bands, implying that octahedral coordinated Zr is present, as shown in Figure 3a. For both Beta-SZ(50) and Beta-SZ(10), the absorption bands derived from charge transfer between Zr and O are present at around 205 nm. This is contributed by isolated tetrahedral Zr⁴⁺, suggesting that Zr was incorporated into zeolite frameworks. The electron state of Zr and Si in Beta and Beta-SZ was investigated using an XPS analysis. The peaks on Zr 3d₄/₂ and 3d₃/₂ are centered at 182.2 and 184.6 eV, respectively, which are attributed to bulk ZrO₂ and the shift to higher binding energy (BE) for Beta-SZ, as shown in Figure 3b. The high BE would be induced by charge transfer among the bonding of Si–O–Zr in Beta-SZ, suggesting that the Zr species might be incorporated into the zeolite framework because Zr has a much lower electronegativity than Si. In addition, curve fitting analysis indicates the presence of bulk ZrO₂ in Beta-SZ(10). While the Si⁴⁺ peak is centered at 103.3 eV for Beta, the peak for Beta-SZ shifted to lower BE, as shown in Figure 3c. This is due to the difference in electronegativity between Si and Zr. Furthermore, clear peaks derived from Si-OH were detected, whereas no clear peak was observed for Beta. Therefore, the incorporation of Zr caused an increase in structural defects of the zeolites. Evidently, curve fitting analysis indicates the presence of a clear different peak for Beta-SZ(10), which is assigned to zircon (ZrSiO₄). Based on these results, it was found that byproducts such as ZrO₂ and ZrSiO₄ are formed using a precursor with an excess amount of Zr. As for Beta-SZ(50), Zr was incorporated into the framework successfully.

The acidity of zeolites is mainly determined by the coordination number of Al species. We measured ²⁷Al MAS NMR spectra for all samples. All catalysts exhibited a specific peak centered at around 54 ppm, as shown in Figure 4. This peak centered at around 54 ppm can be assigned to
tetra-coordinate aluminium, which is incorporated into the framework of the zeolites. Meanwhile, all catalysts also exhibited a broad peak at around 0 ppm. The broad peak at around 0 ppm can be derived from hexa-coordinate aluminium, which is commonly regarded as the extra-framework aluminium species of zeolites.65 Interestingly, by adding Zr, the peak intensity around 0 ppm decreased. Some papers reported that extra-framework aluminium species generated Lewis acidity.48,49 Thus, the number of Lewis acid sites derived from extra-framework aluminium decreased by incorporating Zr into the framework.

To obtain further information regarding acidity, the spectra of Fourier-transform infrared (FTIR) were measured using pyridine as a probe molecule. The measurement has been applied to disclose the detailed acidity of solid materials.66,67 The $\nu_{19b}$ vibration mode of pyridinium ions adsorbed on the Brønsted acid sites appears at 1545 cm$^{-1}$. The band at 1455 cm$^{-1}$ is assigned to the $\nu_{19b}$ mode of coordinated pyridine on the Lewis acid sites.68 These peaks were observed for all samples (Figure 5). The Lewis and Brønsted acid ratios (L/B) were calculated using these FTIR spectra. Beta-SZ(50) showed higher L/B ratio than conventional Beta, as listed in Table 2, suggesting that Lewis acidity was improved by incorporating Zr into the framework.

The thermogravimetric curves during LDPE cracking are measured to investigate catalytic performances of Beta and Beta-SZ.52 LDPE was decomposed by Beta-SZ(50) at lower temperatures than a conventional Beta although the $S_{\text{ext}}$ of Beta-SZ(50) was smaller than that of a conventional Beta (Figure 6). Meanwhile, the LDPE degradation activity of Beta-SZ(10) was drastically lower than Beta because of byproducts.

In order to investigate the effect of Zr, LDPE was also decomposed over a catalyst that was a physical mixture of Beta and ZrO$_2$ in a mass ratio of 1:9; then, the activity was slightly lower than Beta-SZ.
decreased, as shown in Figure S1. In addition, Na-type Beta-SZ(50) showed almost no degradation activity, as shown in Figure S2. Zr-doped Beta had Si–OH, which may work as active sites for LDPE cracking in XPS spectra (Figure 3). However, Beta-SZ(10) was inferior to pristine Beta even though the number of Si–OH sites increased just like Beta-SZ(50). Therefore, the activity was enhanced by the synergetic effect of Brønsted acidity that originated from Al species and Lewis acidic Zr species incorporated into the zeolite framework.

4. CONCLUSIONS

In summary, both Al- and Zr-incorporated Beta zeolite were synthesized using amorphous ZrO2–SiO2. The optimized Zr content in the dry gel allowed the enhancement of Lewis acidity without a significant loss of Brønsted acidity. The enhancement of Lewis acidity probably originated from Zr species incorporated into the zeolite framework. The synthesized catalyst showed superior activity on LDPE cracking to a conventional Beta zeolite due to enhanced Lewis acidity derived from Zr species. Furthermore, a comparative study using a sodium exchanged sample revealed that only Lewis acidity cannot show a high catalytic activity. The activity was enhanced by the synergetic effect of Brønsted acidity that originated from Al species and Lewis acidic Zr species incorporated into the zeolite framework.

Figure 6. TG curves during the degradation of LDPE over Beta and Beta-SZ.

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TG curves obtained in the degradation of LDPE with each sample (PDF)

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