

Article

Kinetic Analysis for the Catalytic Pyrolysis of Polypropylene over Low Cost Mineral Catalysts

Young-Min Kim ^{1,†} , Sumin Pyo ^{2,†}, Hanie Hakimian ^{2,†}, Kyung-Seun Yoo ^{3,†}, Gwang-Hoon Rhee ⁴ and Young-Kwon Park ^{2,*}

- ¹ Department of Environmental Engineering, Daegu University, Gyeongsan 38453, Korea; ymk@daegu.ac.kr
² School of Environmental Engineering, University of Seoul, Seoul 02504, Korea; smpyo2630@gmail.com (S.P.); haniehakimia@gmail.com (H.H.)
³ Department of Environmental Engineering, Kwanwoon University, Seoul 01897, Korea; yooks@kw.ac.kr
⁴ Department of Mechanical and Information Engineering, University of Seoul, Seoul 02504, Korea; ghrhee@uos.ac.kr
* Correspondence: catalica@uos.ac.kr
† Equal contributed co-first authors.

Abstract: A kinetic analysis of non-catalytic pyrolysis (NCP) and catalytic pyrolysis (CP) of polypropylene (PP) with different catalysts was performed using thermogravimetric analysis (TGA) and kinetic models. Three kinds of low-cost natural catalysts were used to maximize the cost-effectiveness of the process: natural zeolite (NZ), bentonite, olivine, and a mesoporous catalyst, Al-MCM-41. The decomposition temperature of PP and apparent activation energy (E_a) were obtained from the TGA results at multiple heating rates, and a model-free kinetic analysis was performed using the Flynn–Wall–Ozawa model. TGA indicated that the maximum decomposition temperature (T_{max}) of the PP was shifted from 464 °C to 347 °C with Al-MCM-41 and 348 °C with bentonite, largely due to their strong acidity and large pore size. Although olivine had a large pore size, the T_{max} of PP was only shifted to 456 °C, because of its low acidity. The differential TG (DTG) curve of PP over NZ revealed a two-step mechanism. The T_{max} of the first peak on the DTG curve of PP with NZ was 376 °C due to the high acidity of NZ. On the other hand, that of the second peak was higher (474 °C) than the non-catalytic reaction. The E_a values at each conversion were also decreased when using the catalysts, except olivine. At <0.5 conversion, the E_a obtained from the CP of PP with NZ was lower than that with the other catalysts: Al-MCM-41, bentonite, and olivine, in that order. The E_a for the CP of PP with NZ increased more rapidly, to 193 kJ/mol at 0.9 conversion, than the other catalysts.



Citation: Kim, Y.-M.; Pyo, S.; Hakimian, H.; Yoo, K.-S.; Rhee, G.-H.; Park, Y.-K. Kinetic Analysis for the Catalytic Pyrolysis of Polypropylene over Low Cost Mineral Catalysts. *Sustainability* **2021**, *13*, 13386. <https://doi.org/10.3390/su132313386>

Academic Editor: Alireza Eivazi

Received: 8 October 2021

Accepted: 29 November 2021

Published: 3 December 2021

Keywords: polypropylene; kinetic analysis; catalytic pyrolysis; bentonite

1. Introduction

Polypropylene (PP) is a well-balanced general-purpose engineering plastic with excellent chemical resistance, high purity, low water absorption, and good electrical insulation properties. Owing to its good physicochemical properties, PP is used widely as a packaging material for consumer goods, internal cases, and containers for electronic products. Worldwide PP production has increased rapidly in recent decades, and its waste exceeds 55 million tons/year globally [1]. Waste PP is difficult to degrade biologically and is easily converted into microplastics, endangering human health. The sudden increase in mask use during the recent COVID-19 pandemic also accelerated the accumulation of PP waste in the environment [2]. Although PP has a good potential to be converted to valuable energy sources or chemical feedstocks, most of it is disposed of by incineration; hence, more desirable treatments are needed [3].

Thermal treatments, such as pyrolysis and gasification, can be considered favorable for achieving a suitable treatment of PP, as well as for production of fuel or chemical feedstock [4]. The minimization of carbon dioxide emissions from the incineration process of PP can be achieved by pyrolysis, and this also mitigates the worldwide global warming issue.

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Pyrolysis is an endothermic process that can decompose polymers into smaller molecules, and PP can be converted to hydrocarbons via random scission during the pyrolysis reaction [5]. On the other hand, the wide carbon number distribution, containing a large amount of heavy wax, is a limitation to commercializing the process [6]. To overcome the low pyrolysis product quality of PP, many researchers have applied various kinds of zeolite catalysts, such as HZSM-5, HY, HBeta, and metal-containing catalysts [7,8]. The successful conversion of low-quality PP pyrolyzates to valuable hydrocarbons, such as aromatic hydrocarbons, can be achieved using these catalysts. Nevertheless, the high cost and the rapid deactivation of synthetic zeolites make the commercialization of the catalytic pyrolysis (CP) process difficult. One of the solutions for decreasing the overall cost of the CP of PP is using inexpensive catalysts. Ryu et al. [9] reported that red mud could be a cost-effective catalyst and can increase the yield of aromatic hydrocarbons from the CP of PP. They also suggested that the co-feeding of PP to the CP of biomass over red mud could enhance the formation of aromatic hydrocarbons. Other natural catalysts, such as natural minerals or zeolites, can decrease the process cost. Ro et al. [10] confirmed that natural catalysts, such as bentonite, dolomite, and olivine, can also increase the cracking efficiency of empty fruit bunches, but studies applying them to the pyrolysis of PP catalysts are limited.

Successful pyrolysis reactor design can be achieved by understanding the target polymer decomposition kinetics, the optimized process conditions, and the product qualities. Understanding the thermal behavior of solid organics during pyrolysis can be achieved by kinetic analysis, using multi-heating rate thermogravimetric analysis (TGA), and a model-free kinetic analysis can be used to estimate the E_a at each conversion, even if the exact reaction model is not known [11]. An improved cracking performance, due to the additional use of catalysts in the pyrolysis of solid organics, can also be determined by comparing the decomposition temperature and E_a .

Vimalathithan et al. [12] evaluated the catalytic effects of different clay nanoparticles on the pyrolysis of PP. They applied four kinds of PP nanocomposites to PP, which were prepared with the addition of four different clay nanoparticles (Cloisite Na⁺, Nanofil5, Bentone 38, and Nanoclay Mica). The activation energy (E_a) for each conversion level, calculated by applying the Ozawa method, indicated that the required E_a to start the decomposition was significantly lower in PP/Cloisite Na⁺; by approximately 124 to 158 kJ/mol [12]. Xu et al. [13] applied TG-FTIR with multi heating rates and model-free kinetic analysis (Ozawa–Flynn–Wall, Kissinger–Akahira–Sunose, and Friedman) to assess the thermal decomposition behavior and E_a of PP and two other typical plastics, including LDPE and PVC. They ranked the degree of difficulty of the pyrolysis process as PVC < PP < LDPE. The E_a values for PP from the three models ranged from 103.02 to 110.75 kJ/mol [13]. In the study implemented by Chi et al. [14], the E_a and T_{max} showed a remarkable reduction when using MCM-41 and Al-MCM-41.

This study examined the degradation kinetics of PP, with both non-catalytic pyrolysis (NCP) and CP with the inexpensive catalysts, natural zeolite (NZ), bentonite, and olivine. A mesoporous zeolite, Al-MCM-41, was also used as a test catalyst. TGA of a PP/catalyst mixture was performed at different heating rates (10, 20, and 30 °C/min) with a nitrogen gas flow rate of 50 ml/min. The Flynn–Wall–Ozawa (FWO) model was applied to calculate the E_a and to evaluate the catalyst performance for PP pyrolysis.

2. Materials and Methods

2.1. Materials and Sample Preparation

PP (particle size < 500 µm) was purchased from Sigma Aldrich. Table 1 lists the physicochemical properties of the utilized PP.

Table 1. Physicochemical properties of the polypropylene used in this study (dry ash free basis).

Proximate Analysis (wt.%)		Ultimate Analysis (wt.%)	
Volatile	99.8	C	85.7
Fixed Carbon	0.2	H	14.3
Sum	100	Sum	100

Al-MCM-41, bentonite, NZ, and olivine were purchased from ACS material and a local catalyst company in Korea. Al-MCM-41 was calcined at 400 °C for 3 h in air. The other catalysts were calcined at 500 °C for 3 h. The Brunauer–Emmett–Teller (BET) surface areas of the catalysts were calculated from the nitrogen adsorption isotherms using a BET surface area and pore size distribution analyzer (BELSorp-Mini II, MicrotracBEL, Osaka, Japan). Before nitrogen adsorption, the catalysts were heated up to 200 °C in vacuum atmosphere to eliminate moisture and impurities. The catalyst acidity was determined by performing a temperature-programmed desorption of ammonia (NH₃-TPD) analysis, according to the following procedure. The catalysts were heated to 500 °C under helium flow (30 mL min^{−1}), to eliminate impurities adsorbed in the catalysts. NH₃ adsorption was performed after cooling down to 100 °C. The amount of absorbed NH₃ in the catalysts was measured using a thermal conductivity detector (TCD), by heating the catalysts from 100 to 500 °C at 10 °C min^{−1} under a helium flow (30 mL min^{−1}).

2.2. Thermogravimetric Analysis

TGA was carried out using a TG analyzer (Pyris 1, Perkin Elmer, Waltham, MA, USA). The non-catalytic thermal conversion was performed by heating 1 mg of PP from 40 °C to 700 °C at heating rates of 10, 20, and 30 °C/min, with a nitrogen flow rate of 50 ml/min. In the case of the catalytic TGA, 6 mg of catalyst/PP mixture (5/1) was heated under the same TGA conditions.

2.3. Kinetic Analysis

The FWO method [15] was used to estimate the change in *E_a* at each conversion during the decomposition of PP. This method gives an estimation of *E_a* without appraising the reaction model function *f(x)*.

To calculate the *E_a* of the reaction, it is important to calculate the *E_a* for each conversion (*x*). The average calculated *E_a* for each conversion gives the *E_a* of the reaction. *x* can be expressed as Equation (1):

$$x = (w_0 - w_t) / (w_0 - w_f) \quad (1)$$

where *w₀*, *w_t*, and *w_f* are initial mass, sample mass in time *t*, and final mass, respectively. The rate of conversion is expressed as follows in Equation (2):

$$dx/dt = k(T) f(x) \quad (2)$$

where *k(T)* represents the reaction rate constant, and *f(x)* represents the function of the reaction model. Meanwhile, *k(T)* can be expressed using the Arrhenius Law, as below in Equation (3):

$$k(T) = A \exp. (-E_a/RT) \quad (3)$$

where *T*, *A*, *R*, and *E_a* represent the absolute temperature (K), pre-exponential factor (min^{−1}), gas constant (8.314 J/mol K), and *E_a* (kJ/mol), respectively. Comparing Equations (2) and (3) gives:

$$dx/dt = A \exp. (-E_a/RT) f(x) \quad (4)$$

Considering the non-isothermal process, which can be expressed as $dx/dT = (dx/dt) (dt/dT)$, Equation (4) can be written as follows:

$$dx/dT = dt/dT A \exp. (-E_a/RT) f(x) \quad (5)$$

By introducing a specific heating rate ($\beta = dT/dt$), Equation (5) is expressed as Equation (6):

$$dx/dT = A/\beta \exp. (-E_a/RT) f(x) \quad (6)$$

By integrating both sides of Equation (6), we can get the following equation:

$$\int_{x_0}^x dx/f(x) = (A/\beta) \int_{T_0}^T \exp(-E_a/RT) dT \quad (7)$$

By applying Doyle's approximation, Equation (7) can be expressed as Equation (8), which is known as the OFW equation [16]:

$$\ln(\beta) = \ln [A E_a/R f(X)] - 5.331 - 1.052 E_a/RT \quad (8)$$

The E_a values can be calculated using the slope, $-1.052 (E_a/T)$, of $\ln(\beta)$ versus $1/T$ plot at each conversion.

3. Results and Discussion

3.1. Characterization of Catalysts

Table 2 shows the BET surface area and average pore size of the catalysts. Al-MCM-41 had the largest BET surface, followed in order by NZ, bentonite, and olivine. Bentonite had the largest pore size among the catalysts, followed in order by olivine, Al-MCM-41, and NZ.

Table 2. BET results and pore properties of the catalysts used in this study.

Catalyst	S_{BET} (m^2/g)	Average Pore Size (nm)
Al-MCM-41	512	2.7
Natural zeolite	157	0.5
Bentonite	23	29.8
Olivine	0.2	7.9

The catalyst acidity was compared using NH_3 -TPD curves (Figure 1), indicating that Al-MCM-41 had the highest acidity among the catalysts, followed in order by NZ and bentonite. Indeed, the NH_3 -TPD curves of Al-MCM-41 and NZ showed two peaks, at a T_{max} of 120–280 °C and T_{max} of 350–470 °C, ascribed to the medium-weak and strong acid sites, respectively [17]. However, only one peak in the range of strong acid sites was observed for bentonite, and no peak was observed for olivine, indicating the very low acidity of olivine.

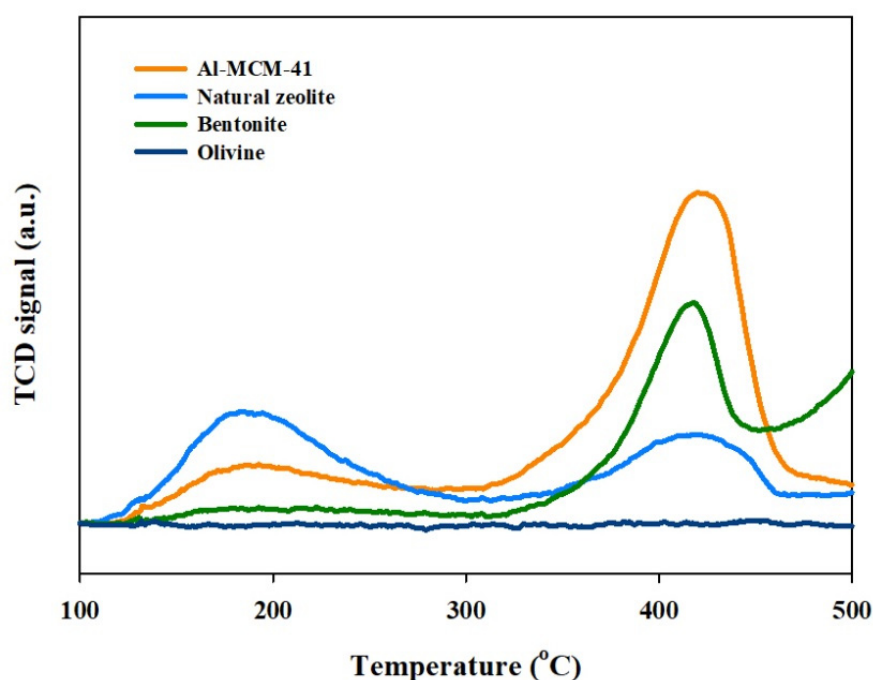
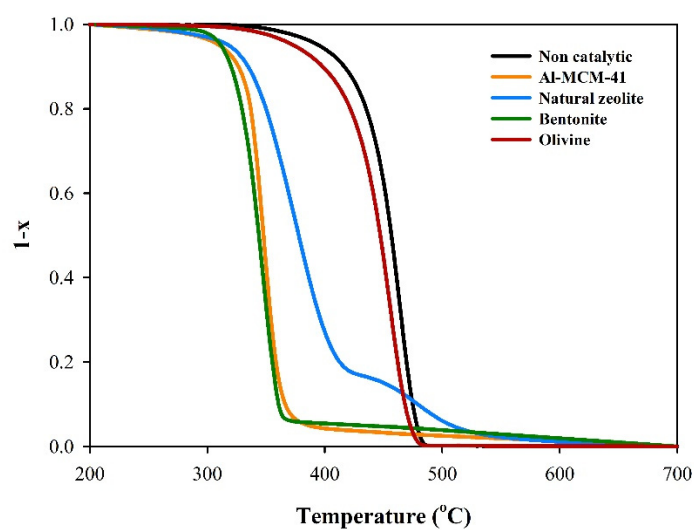


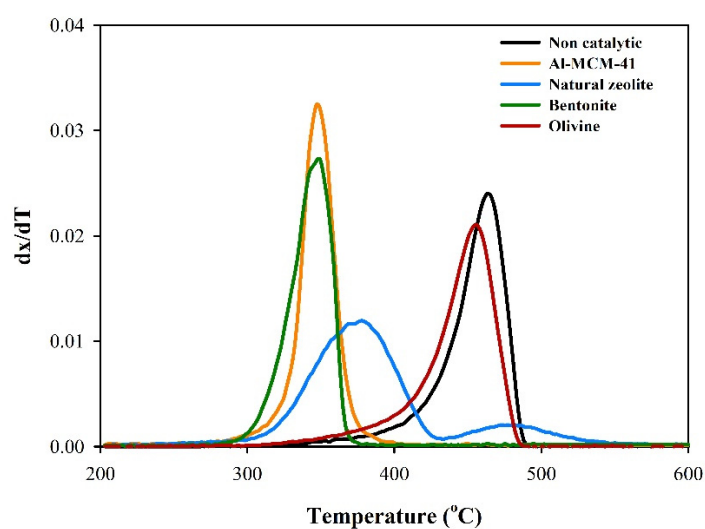
Figure 1. NH_3 -TPD curve of the catalysts used in this study.

3.2. Thermogravimetric Analysis and Kinetic Study

Figure 2 shows the TG and derivative TG (DTG) curves obtained from NCP and CP of PP at $10\text{ }^\circ\text{C}/\text{min}$. As shown in Figure 2, the NCP of PP revealed a sharp DTG curve, and its maximum decomposition temperature (T_{max}) was $464\text{ }^\circ\text{C}$, as demonstrated in Table 3. Although using olivine did not change the original decomposition temperature of PP significantly, the T_{max} of the DTG curve was lowered to $456\text{ }^\circ\text{C}$, suggesting its high catalytic effect, despite a very low acidity (Figure 1). The DTG peak shape for the CP of PP with olivine was similar to that for the thermal decomposition of PP. This suggests that the main reaction pathway in the thermal decomposition of PP, a single-stage reaction consisting of random scission [5], was accelerated when using olivine, without changing the reaction pathway. In comparison to olivine, the CP of PP with Al-MCM-41 revealed a much lower T_{max} ($347\text{ }^\circ\text{C}$). This suggests that Al-MCM-41 had a higher catalytic effect than olivine, owing to its larger BET surface area and higher acidity, as confirmed by Table 1 and Figure 1. Bentonite showed a similar T_{max} ($348\text{ }^\circ\text{C}$) to Al-MCM-41, suggesting its potential use as a cost-effective catalyst in PP decomposition. Similarly, Ro et al. [10] indicated that bentonite had a larger BET surface area ($19\text{ m}^2/\text{g}$) than olivine ($2\text{ m}^2/\text{g}$), and its acidity was also higher, leading to its higher catalytic activity. The DTG curve for the CP of PP over NZ also had a much lower T_{max} than the NCP of PP, but it also had a second DTG peak in the high-temperature region, between 430 and $550\text{ }^\circ\text{C}$. This suggests that NZ can increase the decomposition efficiency of PP at the initial stages, but a much higher heat energy than for a non-catalytic reaction is required for the complete reaction. During the CP of PP, large molecular reaction intermediates can condense in the pores of NZ at a temperature lower than $430\text{ }^\circ\text{C}$ and be re-vaporized at higher temperatures, because of the accelerated secondary cracking and efficient vaporization at elevated temperatures [18].



(a) TG



(b) DTG

Figure 2. TG (a) and DTG (b) curves for NCP and CP of polypropylene at a heating rate of 10 °C/min.**Table 3.** Maximum decomposition temperature ($T_{\max}$) of polypropylene over different catalysts.

Catalyst	$T_{\max}$ (°C)
Non catalytic	464
Al-MCM-41	347
Natural zeolite	1st: 376 2nd: 474
Bentonite	348
Olivine	456

Figure 3 represents the slopes of $\ln(\beta)$ versus $1/T$, with different conversions obtained from the TGA of the NCP and CP of PP. All plots in Figure 3 have a higher linearity ($R^2 > 0.98$), confirming the suitability of the applied kinetic analysis.

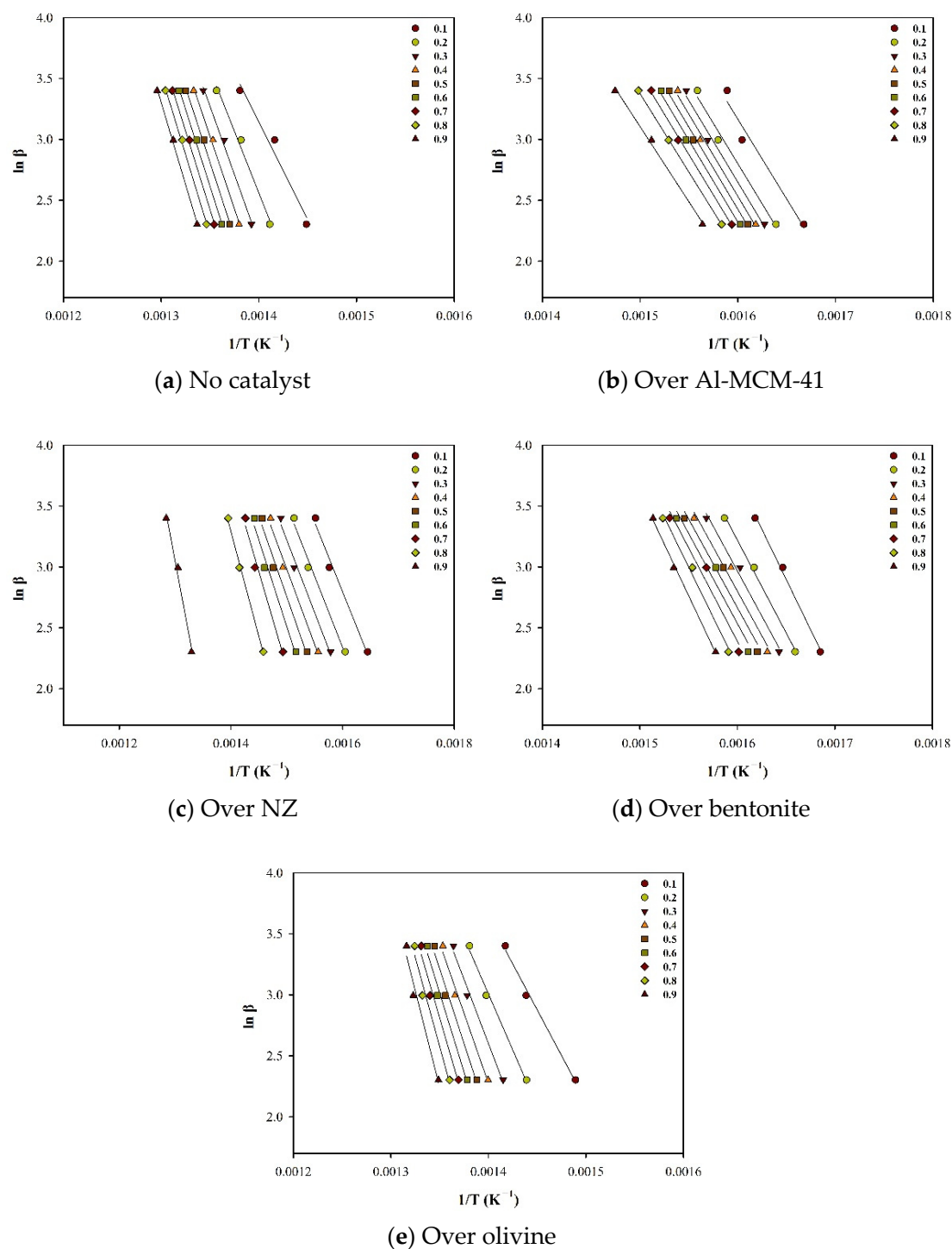


Figure 3. Plots of $\ln(\beta)$ versus $1/T$ with different conversions, using a TGA of the NCP and CP of polypropylene.

Figure 4 shows the E_a at each conversion obtained from the kinetic analysis of the NCP and CP of PP using the Flynn–Wall–Ozawa method. In case of the NCP of PP, the E_a values increased gradually, from 127 kJ/mol at 0.1 conversion to 213 kJ/mol at 0.9 conversion, and its average value was 186 kJ/mol.

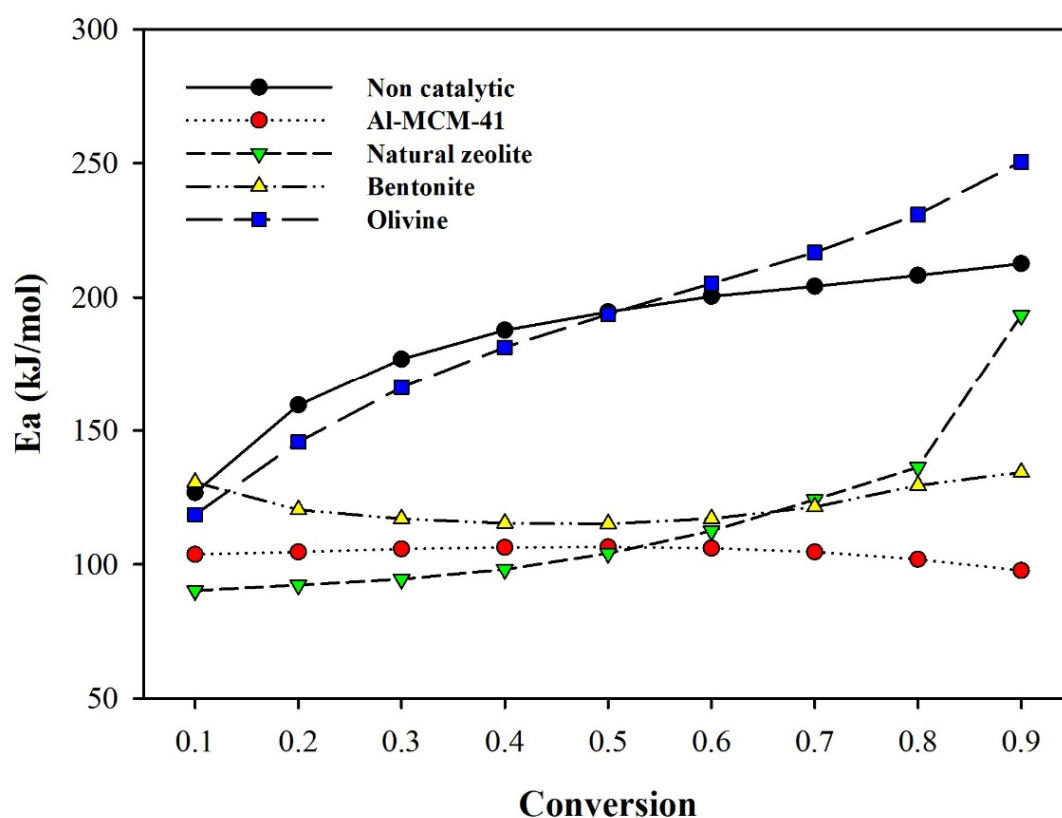


Figure 4. E_a at each conversion for the NCP and CP of PP.

Table 4 presents the kinetic parameters achieved in this study and other similar studies. The CP of PP over olivine revealed lower E_a values at a conversion lower than 0.5. Those at the conversions >0.5 were higher than NCP, suggesting that a high-energy input is also required for the cracking and vaporization of coke deposited on the catalyst [19]. The CP with Al-MCM-41 revealed much lower E_a values (104 kJ/mol) than the NCP at all conversions. This can be explained by the high acidity and BET surface area, which allows a high cracking efficiency, efficient reactant diffusion, and easy vaporization of catalytic reaction intermediates from the catalyst pores, owing to its mesoporosity [20]. Although NZ reduced the E_a of the PP decomposition reaction compared to Al-MCM-41 at conversions <0.5 , the E_a values at conversions >0.5 were much higher than those with Al-MCM-41. Moreover, the E_a value increased to 193 kJ/mol at 0.9 conversion. This suggests that a large molecular catalyst allows for lower E_a values at high conversion rates, because a more efficient vaporization of catalytic reaction intermediates can be achieved using a larger pore catalyst [21]. Although the catalytic TGA of PP over bentonite could not have lower E_a values at lower conversions than NZ, because of its lower acidity, the E_a from 0.7 conversion were lower than those with NZ, suggesting a potential use of bentonite for its stable cracking activity during sequential use.

To determine the catalytic thermal decomposition mechanism of PP, thermal and CP of PP were also performed using a pyrolyzer-GC/MS at 600 °C, as shown in Figure S1 (Supplementary Information). With Al-MCM-41 and bentonite, light hydrocarbons were mainly produced during the pyrolysis of PP, due to their strong acidity (Figure 1) and large pore size (Table 2). Meanwhile, the peak intensities for toluene and xylene on the chromatogram obtained from the Py-GC/MS analysis of PP with NZ were much larger than those obtained with the other catalysts. This suggests that a more effective hydrocarbon pool [25] can be made in the pores of NZ, and this leads to increased aromatic production.

Table 4. Kinetic parameters of decomposition of PP with different catalysts.

Catalyst	T _{max}	E _a	Applied Method	Ref.
Non catalytic	411	114		
BEA zeolite	224	59		
ZSM-5 (SiO ₂ /Al ₂ O ₃ = 12.5)	228	98		[22]
ZSM-5 (SiO ₂ /Al ₂ O ₃ = 25)	264	62		
MOR zeolite	280	51		
Non catalytic	397	-	-	
LZ-Y52 molecular sieve	373	64.6	Ozawa–Flynn–Wall	[23]
		57.5	modified Coats–Redfern	
		57.97	Tang–Wanjuan method	
Non catalytic	376.2	-	-	
10% zeolite mordenite ammonium	359.7	73.3	Ozawa–Flynn–Wall	[24]
		66.1	modified Coats–Redfern	
		65.8	Tang–Wanjuan method	
Non catalytic	464	185.6		
Olivine	456	189.8		
Bentonite	348	122.2	Ozawa–Flynn–Wall	This study
Al-MCM-41	347	104.1		
NZ	1st peak: 376 2nd peak: 474	116.1		

4. Conclusions

This study assessed the feasibility of the natural and cost-effective catalysts, NZ, olivine, and bentonite, for the decomposition of PP by TGA. Among these catalysts, bentonite and NZ were effective at lowering the PP decomposition temperature and E_a values during PP pyrolysis and their performances were comparable with Al-MCM-41. Between NZ and bentonite, NZ showed lower E_a values at the initial stage of PP pyrolysis, but higher E_a values were observed at high conversions, because of its small pore size. Bentonite showed a low and stable cracking efficiency during the PP decomposition stage, suggesting its potential use as a stable catalyst for PP pyrolysis.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/su132313386/s1>, Table S1: GC/MS conditions used in this study, Figure S1: Micropyrolyzer-GC/MS chromatograms for catalytic pyrolysis of polypropylene.

Author Contributions: Conceptualization, Y.-K.P.; formal analysis, K.-S.Y.; investigation, G.-H.R.; data curation, Y.-M.K., S.P. and H.H.; writing—original draft preparation, Y.-M.K., S.P. and H.H.; writing—review and editing, Y.-K.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Research Foundation of Korea (NRF-2019R1F1A1061554). This work was also supported through the Technology Innovation Program (20015401) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea). This work was also supported by Korea Environment Industry & Technology Institute (KEITI) through Post Plastic, a specialized program of the Graduate School funded by Korea Ministry of Environment (MOE).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Bora, R.R.; Wang, R.; You, F. Waste polypropylene plastic recycling toward climate change mitigation and circular economy: Energy, environmental, and technoeconomic perspectives. *ACS Sustain. Chem. Eng.* **2020**, *8*, 16350–16363. [\[CrossRef\]](#)
- Fadare, O.O.; Okoffo, E.D. Covid-19 face masks: A potential source of microplastic fibers in the environment. *Sci. Total Environ.* **2020**, *737*, 140279. [\[CrossRef\]](#) [\[PubMed\]](#)
- Lee, H.W.; Park, Y.-K. Catalytic pyrolysis of polyethylene and polypropylene over desilicated beta and Al-MSU-F. *Catalysts* **2018**, *8*, 501. [\[CrossRef\]](#)
- Wu, C.; Williams, P.T. Hydrogen production by steam gasification of polypropylene with various nickel catalysts. *Appl. Catal. B Environ.* **2009**, *87*, 152–161. [\[CrossRef\]](#)
- Kim, H.-S.; Kim, S.; Kim, H.-J.; Yang, H.-S. Thermal properties of bio-flour-filled polyolefin composites with different compatibilizing agent type and content. *Thermochim. Acta* **2006**, *451*, 181–188. [\[CrossRef\]](#)
- Kassargy, C.; Awad, S.; Burnens, G.; Kahine, K.; Tazerout, M. Gasoline and diesel-like fuel production by continuous catalytic pyrolysis of waste polyethylene and polypropylene mixtures over USY zeolite. *Fuel* **2018**, *224*, 764–773. [\[CrossRef\]](#)
- Santos, B.P.S.; Almeida, D.; Maria de Fatima, V.M.; Henriques, C.A. Petrochemical feedstock from pyrolysis of waste polyethylene and polypropylene using different catalysts. *Fuel* **2018**, *215*, 515–521. [\[CrossRef\]](#)
- Lee, H.W.; Choi, S.J.; Jeon, J.-K.; Park, S.H.; Jung, S.-C.; Park, Y.-K. Catalytic conversion of waste particle board and polypropylene over H-beta and HY zeolites. *Renew. Energy* **2015**, *79*, 9–13. [\[CrossRef\]](#)
- Ryu, S.; Lee, H.W.; Kim, Y.-M.; Jae, J.; Jung, S.-C.; Ha, J.-M.; Park, Y.-K. Catalytic fast co-pyrolysis of organosolv lignin and polypropylene over in-situ red mud and ex-situ HZSM-5 in two-step catalytic micro reactor. *Appl. Surf. Sci.* **2020**, *511*, 145521. [\[CrossRef\]](#)
- Ro, D.; Kim, Y.-M.; Lee, I.-G.; Jae, J.; Jung, S.-C.; Kim, S.C.; Park, Y.-K. Bench scale catalytic fast pyrolysis of empty fruit bunches over low cost catalysts and HZSM-5 using a fixed bed reactor. *J. Clean. Prod.* **2018**, *176*, 298–303. [\[CrossRef\]](#)
- Opfermann, J.R.; Kaisersberger, E.; Flammersheim, H.J. Model-free analysis of thermoanalytical data—advantages and limitations. *Thermochim. Acta* **2002**, *391*, 119–127. [\[CrossRef\]](#)
- Vimalathithan, P.K.; Barile, C.; Casavola, C.; Arunachalam, S.; Battisti, M.G.; Friesenbichler, W.; Vijayakumar, C.T. Thermal degradation kinetics of polypropylene/clay nanocomposites prepared by injection molding compounder. *Polym. Compos.* **2019**, *40*, 3634–3643. [\[CrossRef\]](#)
- Xu, F.; Wang, B.; Yang, D.; Hao, J.; Qiao, Y.; Tian, Y. Thermal degradation of typical plastics under high heating rate conditions by TG-FTIR: Pyrolysis behaviors and kinetic analysis. *Energy Convers. Manag.* **2018**, *171*, 1106–1115. [\[CrossRef\]](#)
- Chi, Y.; Xue, J.; Zhuo, J.; Zhang, D.; Liu, M.; Yao, Q. Catalytic co-pyrolysis of cellulose and polypropylene over all-silica mesoporous catalyst MCM-41 and Al-MCM-41. *Sci. Total Environ.* **2018**, *633*, 1105–1113. [\[CrossRef\]](#) [\[PubMed\]](#)
- Aboullkas, A.; El harfi, K.; El Bouadili, A. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. *Energy Convers. Manag.* **2010**, *51*, 1363–1369. [\[CrossRef\]](#)
- Ali, G.; Nisar, J.; Iqbal, M.; Shah, A.; Abbas, M.; Shah, M.R.; Rashid, U.; Bhatti, I.A.; Khan, R.A.; Shah, F. Thermo-catalytic decomposition of polystyrene waste: Comparative analysis using different kinetic models. *Waste Manag. Res.* **2020**, *38*, 202–212. [\[CrossRef\]](#) [\[PubMed\]](#)
- Pham, S.T.; Nguyen, M.B.; Le, G.H.; Nguyen, T.D.; Pham, C.D.; Le, T.S.; Vu, T.A. Influence of Brønsted and Lewis acidity of the modified Al-MCM-41 solid acid on cellulose conversion and 5-hydroxymethylfurfuran selectivity. *Chemosphere* **2021**, *265*, 129062. [\[CrossRef\]](#)
- Salman, M.; Nisar, S.; Hussain, Z.; Salman, H.; Kazimi, M.R. TGA-DSC: A screening tool for the evaluation of hydrocracking catalyst performance. *Am. J. Anal. Chem.* **2015**, *6*, 364–375. [\[CrossRef\]](#)
- Güleç, F.; Meredith, W.; Snape, C.E. Progress in the CO₂ Capture Technologies for Fluid Catalytic Cracking (FCC) Units—A Review. *Front. Energy Res.* **2020**, *8*, 62. [\[CrossRef\]](#)
- Locus, R.; Verboekend, D.; Zhong, R.; Houthoofd, K.; Jaumann, T.; Oswald, S.; Giebler, L.; Baron, G.; Sels, B.F. Enhanced acidity and accessibility in Al-MCM-41 through aluminum activation. *Chem. Mater.* **2016**, *28*, 7731–7743. [\[CrossRef\]](#)
- Elfadly, A.; Zeid, I.; Yehia, F.; Abouelela, M.; Rabie, A. Production of aromatic hydrocarbons from catalytic pyrolysis of lignin over acid-activated bentonite clay. *Fuel Process. Technol.* **2017**, *163*, 1–7. [\[CrossRef\]](#)
- Durmuş, A.; Koç, S.N.; Pozan, G.S.; Kaşgöz, A. Thermal-catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites. *Appl. Catal. B Environ.* **2005**, *61*, 316–322. [\[CrossRef\]](#)
- Khan, M.A.; Nisar, J.; Iqbal, M.; Shah, A.; Khan, R.A.; Bhatti, I.A.; Amin, R. Pyrolysis of polypropylene over a LZ-Y52 molecular sieve: Kinetics and the product distribution. *Iran. Polym. J.* **2019**, *28*, 839–847. [\[CrossRef\]](#)
- Nisar, J.; Khan, M.A.; Ali, G.; Iqbal, M.; Shah, A.; Shah, M.R.; Sherazi, S.T.H.; Shah, L.A.; Rehman, N.U. Pyrolysis of polypropylene over zeolite mordenite ammonium: Kinetics and products distribution. *J. Polym. Eng.* **2019**, *39*, 785–793. [\[CrossRef\]](#)
- Kim, B.-S.; Kim, Y.-M.; Lee, H.W.; Jae, J.; Kim, D.H.; Jung, S.-C.; Watanabe, C.; Park, Y.-K. Catalytic Copyrolysis of Cellulose and Thermoplastics over HZSM-4 and HY. *ACS Sustain. Chem. Eng.* **2016**, *4*, 1354–1363. [\[CrossRef\]](#)