

CATALYZED DEGRADATION OF POLYETHYLENE TEREPHTHALATE

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Abstract In this research catalyzed degradation of polyethylene terephthalate was performed. For that purpose, ZSM-5 zeolite was synthesized as an acid catalyst. For its characterization N_2 adsorption, scanning electron microscopy, NH_3 temperature programmed desorption, differential scanning calorimetry, thermogravimetric analysis, dynamic light scattering, and Fourier transform infrared spectroscopy were utilized. Degradation reactions were performed in high pressure crucibles using differential scanning calorimeter at different temperatures (200, 250 and 300) °C and time intervals (2.5, 5, 10 and 15) min. Samples were analyzed using high performance liquid chromatography coupled with UV-VIS detector. The results revealed that the highest conversion was achieved at 300 °C and 10 min. The analysis of obtained results showed that despite the differences in conversions being not as high as expected, reactions with the catalyst were slightly more effective than without it. For the future work, we plan to finetune the synthesis procedure to obtain more active catalyst. And for the upgrade of the study the kinetic analysis of the reaction will be conducted.

Keywords:
degradation,
catalyst,
ZSM-5,
polyethylene
terephthalate,
DSC

1 Introduction

Polymers represent materials, which we use daily practically everywhere in our lives. Their usage in food, cosmetics, building and electro industry has risen significantly in the past decades. (Namazi, 2017)

Life without synthetic materials is not imaginable. Population growth, higher life standard and the revolution of technology are the reasons for high production of polymers. Most of the produced plastic and polymer products are not biodegradable, which has a significant impact on the environmental pollution. Researchers are looking for an economical, technological and environmental solution for a replacement of polymer materials and its recycling or transformation to other useful products. (Manfra, 2021 and Kumar Gupta, 2022)

Polyethylene terephthalate (PET), which belongs to the polyester family, is a widely used linear semi-crystalline thermoplastic polymer due to its favorable mechanical and thermal properties. It belongs to the unbranched polymers obtained by the esterification reaction between ethylene glycol (EG) and terephthalic acid (TPA) or by trans-esterification between ethylene glycol and dimethyl terephthalate. Due to its advantages and useful properties (flexibility, recyclability, electrical-insulating properties, high mechanical strength, low weight, resistance to alcohols and aliphatic hydrocarbons), it is commercially found mainly in packaging, fibers and electronics. It is more suitable for recycling compared to other alternative materials. The most used recycling methods are hydrolysis and mechanical mixing. In chemical recycling, TPA and EG are formed as hydrolysis products. From an economic and environmental point of view, mechanical recycling is more often used. (PET, 2022 and Yan, 2023)

The aim of this study was to synthesize a new acid catalyst, which would be appropriate for PET degradation. Advanced analytical techniques were used for catalyst characterization.

2 Materials and methods

2.1 Materials

All the reagents and solvents used were of analytical grade. Sodium hydroxide (NaOH, 99 %), Sodium aluminate (NaAlO_2 , Al_2O_3 : 50-56 %, Na_2O : 37-45 %), Tetrapropylammonium bromide (TPABr, 98 %), Bis(2-hydroxyethyl) terephthalate (BHET), *Trifluoroacetic acid* (TFA, 99 %) were purchased from Sigma-Aldrich, Ammonium nitrate (NH_4NO_3 , 99 %) from Kemika, Tetraethyl orthosilicate (TEOS, 98 %) from J&K Scientific Ltd., Polyethylene terephthalate (PET) from Melanin, and Acetonitrile (ACN 99,9 %) from Honeywell.

2.2 Methods

2.2.1 Catalyst synthesis

0.05 g of NaAlO_2 and 0.6 g of NaOH were dissolved in 101.25 mL of deionized water. 2.1 g of TPABr and 6.425 g of TEOS were added to the solution and stirred overnight. Then the solution was transferred into an autoclave and aged for 48 h at 180 °C. Afterwards, the solution was filtered, solid product washed with deionized water, dried at 100 °C and then calcined for 6 h at 550 °C. Ion exchange of solid product was performed with 500 mL of 0.2 M NH_4NO_3 solution during stirring for 3 h at 80 °C. The particles were filtered and dried. The process of ion exchange was repeated three times. At the end the solid product was calcined for 6 h at 550 °C.

2.2.2 Catalyst characterization

The synthesized catalyst was characterized by nitrogen adsorption-desorption (BET), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), dynamic light scattering (DLS), thermogravimetric analysis (TGA), and temperature programmed desorption (TPD).

2.2.3 Polyethylene terephthalate degradation

Polyethylene terephthalate degradation reactions were performed in a differential scanning calorimeter from Mettler Toledo (DSC3). The reactions were carried out in a small high- pressure stainless-steel reactor with a volume of 30 μL , at temperatures 200, 250 and 300 $^{\circ}\text{C}$ and time 2.5, 5, 10 and 15 min. At each temperature and time, the reaction was performed with and without the catalyst. 5 mg of polyethylene terephthalate (PET) and 2.5 mg of the ZSM-5 catalyst were weighed into the reactor. Then 20 μL of deionized water was added. The reactor used for PET degradation reaction is shown in Figure. After a certain time, 10 μL of the sample was withdrawn from the reactor and diluted with 490 μL of mobile phase. It was further used for the analysis.



Figure 1: High-pressure stainless-steel reactor with the sample.

Source: own.

2.2.4 Analysis

The analyses of TPA and intermediate BHET were performed on a Hewlett Packard series 1100 high performance liquid chromatograph HPLC coupled to a UV-VIS detector. The separation of compounds was performed on an Agilent Eclipse XD8-C18 chromatography column (4.6 x 250 mm, 5 μm) at 30 $^{\circ}\text{C}$. The mobile phase consisted of two solvents, A: acetonitrile (ACN) and B: water (0.1 % TFAA), (A:B=25:75). The flow rate through the column was 1 mL min^{-1} . The detection was performed at 240 nm. The samples were washed from reactor with 0,5 % NaOH and diluted to 2 mL. This solution

was then further diluted (50 μL of sample and 1450 μL of mobile phase) and filtered through a 0.22 μm PES filter. The TPA and intermediate BHET concentrations were obtained from calibration curves.

3 Results and discussion

3.1.1 Catalyst characterization

The nitrogen adsorption/desorption isotherms (Figure 2) of the catalyst show type IV isotherms with a clear hysteresis loop at relative pressures of $p/p_0 = (0.3 - 1.0)$. The determined BET surface area was 360.6 m^2/g , pore size 2.0 nm and pore volume 0.18 cm^3/g . The synthesized catalyst belongs to mesoporous material with a relatively large surface area.

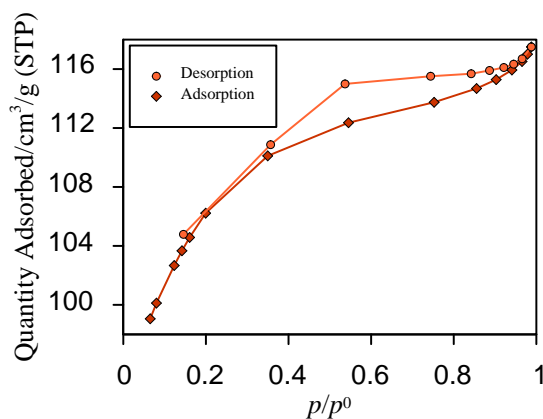


Figure 2: BET.

Source: own.

From the FTIR spectra it was not possible to determine the presence of specific functional groups.

The morphology of the synthesized catalyst was observed by scanning electron microscopy (SEM) and the images obtained are shown in Figure 3. We can see that the catalyst forms clusters of several smaller particles. From higher magnifications it can be seen that the size of one particle is about 0.5 μm , which is in agreement with DLS measurement, where the average particle size was determined to be 0.57 μm .

From the results of the TGA measurement we could determine only one step change at the beginning of the measurement to around 200 °C, which is attributed to the loss of bound water.

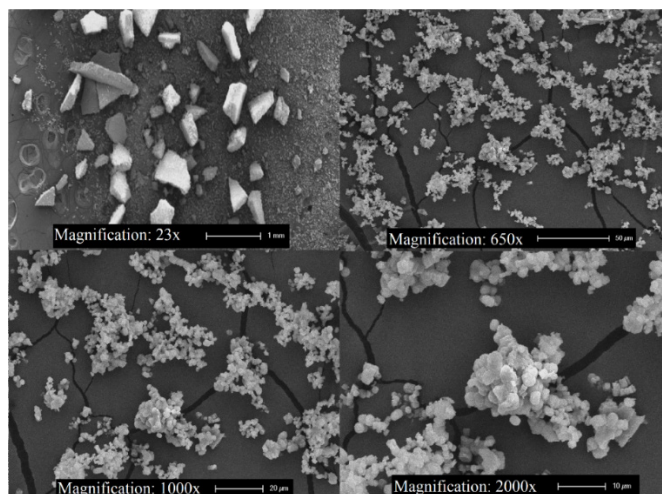


Figure 3: SEM image of ZSM-5 catalyst.

Source: own.

In order to determine the acid properties of synthesized catalyst temperature programmed desorption of NH_3 was performed. From the response (Figure 4) it is clear that there are many weak acid sites presented (peak around 120 °C) and only few strong acid ones (peak around 450 °C).

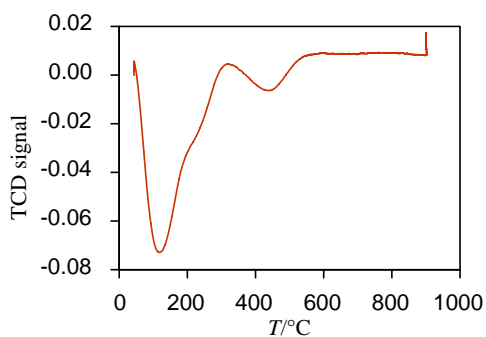


Figure 4: TPD of NH_3 .

Source: own.

3.1.2 Polyethylene terephthalate degradation

The reactions of PET degradation were performed at different temperatures (200, 250 and 300 °C) and time periods (2.5, 5, 10 and 15 min). The obtained concentrations of TPA and BHET at 200 °C are shown in Figure 5.

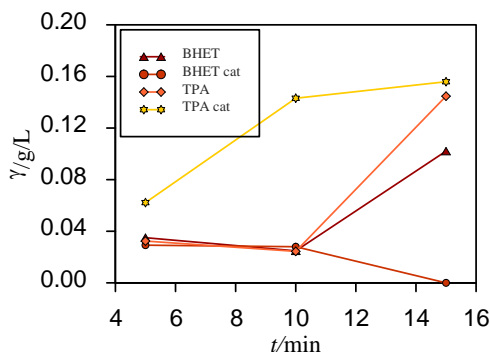


Figure 5: Concentrations of TPA and BHET regarding time at 200 °C.

Source: own.

It is known that during the degradation of PET two intermediates BHET and MHET are first formed and then the degradation proceeds towards to TPA. Because of the inaccessibility of MHET we were only able to determine the concentrations of BHET and TPA. We observed that at all temperatures the concentrations of TPA and BHET increase with increasing time of the reaction. But the increase in the concentrations is more pronounced with increasing temperature. We also confirmed that the synthesized solid acid catalyst was active during the degradation of PET. Namely, for most reactions performed with the catalyst the concentrations of formed TPA were higher than for those without the catalyst.

4 Conclusion

The reactions of PET degradation took place in a differential scanning calorimeter. Further, the catalyst characterization using different characterization methods was performed. It was confirmed that synthesized catalyst has acid properties. The reaction with a catalyst was more effective at a certain temperature than without it, yet the achieved conversions were lower than expected. The conclusion drawn from this study is that

synthesized catalyst is not efficient enough to be used in the degradation of polyethylene terephthalate. In the comparison between the use of the catalyst and the increase of the reaction temperature, it was found that in our case the temperature has a greater influence on the reaction conversion.

Acknowledgments

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