ACID- AND BASE-FREE DEPOLYMERIZATION OF POLY(ETHYLENE TEREPHTHALATE): A REVIEW ON HOMOGENEOUS IRON-CATALYZED CHEMICAL RECYCLING

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Abstract— Chemical recycling of poly(ethylene terephthalate) (PET) is increasingly recognized as a key technology for achieving a circular plastics economy. Among the various chemical recycling routes, depolymerization via transesterification offers the possibility of recovering PET monomers with high purity. This review focuses on the recent work by Nomura et al. on the acid- and base-free depolymerization of PET using ethanol and homogeneous iron catalysts, specifically $FeCl_3$ and $FeBr_3$. The reviewed study demonstrates highly selective conversion of PET into diethyl terephthalate (DET) and ethylene glycol (EG) under relatively mild conditions, with excellent applicability to textile waste and mixed-material streams. The catalytic system shows remarkable selectivity, operational simplicity, and potential industrial relevance due to the use of inexpensive and commercially available catalysts. This review discusses the reaction concept, catalytic performance, scope, limitations, and significance of this approach in comparison with established PET recycling methods.

Keywords— Chemical recycling, Depolymerization, PET, Textile waste, Transesterification

1. Introduction

The widespread use of synthetic polymers has led to a rapid increase in plastic waste, raising serious environmental and economic concerns. Poly(ethylene terephthalate) (PET) is one of the most extensively produced polyesters, widely applied in packaging, bottles, and textile fibers. Although mechanical recycling of PET is practiced on an industrial scale, it often results in material downcycling and inferior product quality compared to virgin polymers. Chemical recycling, defined as the conversion of polymers back into monomers or valuable chemicals, has gained increasing attention as a route toward closed-loop material cycles. Conventional chemical depolymerization methods for PET, such as glycolysis, methanolysis, and hydrolysis, typically require strong acids or bases, high temperatures and pressures, or excess additives, which complicate product separation and increase process costs. In this context, the development of efficient, selective, and additive-free catalytic systems is highly desirable. The work reviewed here presents a homogeneous iron-catalyzed depolymerization of PET with ethanol that proceeds without acids or bases, offering a simplified and sustainable approach to chemical recycling.

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2. CHEMICAL DEPOLYMERIZATION OF PET: STATE OF THE ART

Numerous catalytic systems for PET depolymerization have been reported, including metal salts, organocatalysts, ionic liquids, and heterogeneous metal oxides. While high depolymerization efficiencies have been achieved, many processes rely on harsh reaction conditions or produce complex product mixtures that require extensive purification steps. Transesterification-based depolymerization is particularly attractive because it directly yields esterified terephthalate derivatives suitable for repolymerization. However, traditional transesterification routes often depend on strong bases or expensive catalysts, limiting large-scale applicability.

Nomura *et al.* build on earlier work in transesterification catalysis and demonstrate that simple iron(III) halides can act as effective homogeneous catalysts for PET depolymerization, thereby addressing several limitations of existing methods.

3. IRON-CATALYZED DEPOLYMERIZATION OF PET WITH ETHANOL

3.1 Reaction Concept and Catalysts

The reviewed study employs $FeCl_3$ and $FeBr_3$ as homogeneous Lewis-acid catalysts for the depolymerization of PET via transesterification with ethanol. The reaction converts PET exclusively into diethyl terephthalate (DET) and ethylene glycol (EG), which are both valuable monomers for PET synthesis. Importantly, the process is entirely acid- and base-free, simplifying downstream processing.

3.2 Catalytic Performance

Under optimized conditions (160–180 °C, 1.0–5.0 mol% catalyst), PET conversion exceeds 99%, with DET yields of 98–99%. $FeCl_3$ exhibits higher catalytic activity than $FeBr_3$, particularly at lower temperatures. Spectroscopic and chromatographic analyses confirm the exclusive formation of DET and EG, with no detectable side products. Kinetic observations suggest that PET initially degrades into oligomeric intermediates, which are subsequently converted into DET over time. This mechanistic insight aligns with earlier studies on transesterification-driven polyester depolymerization.

4. APPLICATION TO TEXTILE AND MIXED PLASTIC WASTE

A major strength of the reviewed work is its applicability to real waste streams. PET-containing textile materials, including PET/cotton blends, were successfully treated under the same reaction conditions. PET was quantitatively depolymerized, while cotton fibers were fully recovered without chemical degradation. Furthermore, the method enables selective depolymerization of PET from mixtures containing polyethylene (PE), demonstrating a promising route for separating polyesters from polyolefin-rich waste. Such selectivity is highly advantageous for recycling complex post-consumer waste materials.

5. Conclusion

The iron-catalyzed, acid- and base-free depolymerization of PET with ethanol represents a significant advancement in chemical recycling technology. The use of inexpensive, commercially available catalysts, combined with high selectivity and operational simplicity, highlights the industrial potential of this approach. Particularly noteworthy is the successful application to textile waste and mixed-material systems, which remain major challenges in current recycling infrastructures. While reaction temperatures and times remain moderate to high, the overall process efficiency and product purity make this method a strong candidate for future closed-loop PET recycling. Continued catalyst development may further reduce energy demands and enhance process sustainability.

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