



Manganese-, cobalt-, and zinc-based mixed-oxide spinels as novel catalysts for the chemical recycling of poly(ethylene terephthalate) via glycolysis

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ABSTRACT

Chemical recycling of post-consumer poly(ethylene terephthalate) (PET) into useful feedstock was carried out in the presence of novel mesoporous metal oxide spinel catalysts. ZnO (hexagonal), metal oxide spinels (Co_3O_4 and Mn_3O_4), and mixed metal oxide spinel (ZnMn_2O_4 , CoMn_2O_4 , and ZnCo_2O_4) catalysts were synthesised via the precipitation or co-precipitation method. The structural, textural, and acidity properties of the materials were examined using various characterisation tools, such as XRD, SEM/EDX, TEM, FT-IR, NH_3 -TPD, and BET surface area analyser. The depolymerisation of waste PET (mostly soft-drink bottles) to the monomer bis(2-hydroxyethyl) terephthalate (BHET) via glycolysis was performed using excess ethylene glycol (EG) in the presence of fabricated metal oxides as transesterification catalysts. The effect of different parameters, such as temperature, catalyst type, reaction time, EG/PET molar ratio, and catalyst/PET weight ratio, on the monomer yield were investigated. The results revealed that the catalyst that yielded the highest amount of BHET (92.2 mol%) under mild reaction conditions (260 °C and 5.0 atm) was zinc manganite tetragonal spinel (ZnMn_2O_4), which has tetrahedral Zn^{+2} ion and octahedral Mn^{+3} ion coordination with the spinel crystal structure. The high catalytic activity of this spinel may be attributed to its greater surface area, the presence of mild and strong acid sites, and its overall higher concentration of acid sites. Furthermore, the ZnMn_2O_4 structural properties were examined, and it was determined that the $\text{Zn}^{+2}/\text{Mn}^{+3}$ metal cations pair, their positioning in the crystal structure, and that the spinel geometry has a pronounced effect on the catalytic efficiency. The monomer, dimer, and oligomers were separated and characterised by thermal (DSC and TGA) and structural (NMR) analyses, which confirmed the purity and structure of the monomer and dimer. Based on the experimental observations, a reaction mechanism was also proposed. In conclusion, the present approach was an attempt to demonstrate a process consisting of a set of new catalysts with optimised process conditions for the maximum production of highly pure BHET.

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1. Introduction

Polyesters are the most significant and cost-effective class of polymers. The versatility of the ester bond and its ability to undergo hydrolysis, alcoholysis, ammonolysis, and aminolysis make polyesters one of the preferred materials for recycling. The overall world production of polyesters was 25–30 million tons in 2000;

this value increased to 55 million tons in 2012 and mostly consisted of polyethylene terephthalate (PET). Polyester consumption has increased substantially in fibres and moulding resins due to the strong demand for textile applications, as well as in food packaging and bottle markets for glass replacement [1]. Due to the tremendous increase in consumption, the most viable solution for sustainability is economical recycling of polyesters to preserve resources and the environment.

PET has the second highest (second to aluminium) scrap value as a recycled material. There are four distinct approaches (primary, secondary, tertiary and quaternary) by which post-consumer PET

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can be recycled [2]. Among these approaches, the one that is most suitable from sustainability point of view is tertiary (chemical) recycling because this process generates the monomers from which the polymer was originally fabricated [3]. Chemical recycling of post-consumer PET into useful feedstock is considered to be an axiomatic approach to green sustainability. It involves the chain scission of the polymer with the help of a solvent, and the process is termed 'solvolysis' [4]. The solvolysis processes, such as methanolysis [5,6], hydrolysis [7–9], glycolysis [10], and aminolysis [11], have been extensively studied and reviewed in the literature [12]. Glycolysis consists of the insertion of ethylene glycol into PET chains to produce BHET along with the dimer and oligomers. The glycolysis reaction products can be used for the manufacturing of unsaturated polyester resins, copolyesters, polyurethanes and hydrophobic textile dyestuffs [13]. Moreover, the BHET produced through glycolysis can be added to fresh BHET, and the mixture can be used in either of the two PET production (DMT-based or TPA-based) lines.

Glycolysis without a catalyst is an extremely sluggish process. There has been a strong interest in the development of highly active transesterification catalysts for the depolymerisation of PET to BHET. A large number of catalysts in the form of metal salts, such as acetates [14–17], chlorides [18], hydroxides [19,20], carbonates [21], sulphates [13,19], and phosphates [22], have been extensively studied over the last two decades. Most of these salts are soluble in ethylene glycol, are difficult to separate after the depolymerisation reaction, and require an additional unit operation (distillation) in the chemical process. It has also been noted that the zinc salts do not increase the glycolysis rate at temperatures above 245 °C, which limits their usage at the moderately high temperatures applied to decrease the overall reaction time [23]. Recently, a new series of glycolysis catalyst, including ionic liquids [23,24] and metal oxides [25,26], have been reported. Additionally, a different approach using microwave irradiation in PET glycolysis has also been studied [20]. The synthesis of ionic liquids is cumbersome compared to the synthesis of metal oxides. Our group recently reported the use of metal oxide-doped silica nanoparticles as effective catalysts for PET glycolysis for the first time [25,26]. The results were promising, with BHET yields above 90 mol%. These catalysts were insoluble in EG and acted heterogeneously when the PET was in the molten state.

Metal oxides exhibit a wide range of applications, from the processing sector (catalysis) to the electronics industry (electrodes and superconductors). Using metal oxides as glycolysis catalysts could be a better option than using conventional catalysts with regard to high monomer yield, high mechanical strength, high melting points, flexibility of usage in fixed and fluidised beds, possibility of regeneration, ease of separation, and long shelf life. Pure metal oxides and their mixed-oxide spinels may possess entirely different characteristics due to their physical, physicochemical, textural, and structural properties, which lead to entirely different catalytic properties [27]. The use of mixed-oxide spinels as glycolysis catalysts has not yet been investigated.

Spinel, which have the general formula AB_2O_4 , represent an important class of mixed metal oxides in which A and B are divalent (A^{+2}) and trivalent (B^{+3}) atoms with tetrahedral and octahedral coordination in the crystal structure, respectively. There are two main classes of spinels: normal and inverse. The spinel structure crystallises in either the cubic or tetragonal structure. In the cubic structure, the A^{+2} reside on tetrahedral sites, while the B^{+3} reside on octahedral sites. The tetragonal structure is a deformed form of the cubic structure resulting from deformation in the octahedra because of Jahn–Teller interactions [28]. The mixed metal oxide spinels displayed higher catalytic activity in various applications, such as CO oxidation [29], hydrocarbon combustion [30], and redox

reactions of several organic compounds [31]; however, their utilisation as transesterification catalysts for glycolysis reactions has yet to be fully explored.

In the present study, pure oxides (ZnO , Co_3O_4 , and Mn_3O_4) and mixed-oxide spinel ($ZnMn_2O_4$, $CoMn_2O_4$, and $ZnCo_2O_4$) catalysts were synthesised by a simple precipitation or co-precipitation method. A series of experiments was conducted to investigate the effect of reaction parameters, such as temperature, time, EG/PET mole ratio, and catalyst/PET weight ratio. Attempts were made to effectively separate the BHET from the glycolysis reaction products. The catalysts were characterised by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), ammonia temperature-programmed desorption (NH_3 -TPD), and BET surface area analysis, while the monomer BHET and dimer were characterised by high performance liquid chromatography (HPLC), differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), and nuclear magnetic resonance spectroscopy (NMR). The oligomers produced with varying reaction times were characterised by DSC, and a reaction mechanism was also proposed.

2. Experimental

2.1. Materials

PET waste consisting mostly of post-consumer soft-drink bottles was collected, washed, dried, and cut into small pieces. These pieces were mixed with dry ice and ground to a fine powder with an average particle size of less than 200 μm . The powder PET number-average ($MW_n = 28,000$) and weight-average ($MW_w = 59,000$) molecular weights were determined by gel permeation chromatography (GPC). Ammonium hydroxide (NH_4OH), manganese (II) nitrate hydrate ($Mn(NO_3)_2 \cdot xH_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), anhydrous EG, dimethylsulfoxide (DMSO-d₆), and standard BHET were purchased from Sigma–Aldrich. Tetrahydrofuran (THF) for HPLC was purchased from J.T. Baker. All reagents were used as purchased without further purification.

2.2. Catalysts synthesis

Pure metal oxides were synthesised by a simple precipitation method. Briefly, a 1.0 M solution of a salt precursor ($Mn(NO_3)_2 \cdot xH_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, or $Co(NO_3)_2 \cdot 6H_2O$) was mixed with 0.1 M ammonium hydroxide until the pH of the resulting solution became 9.0. The precipitates of the corresponding metal hydroxides were filtered, washed with water, and dried at 100 °C for 8 h. Pure metal oxide was obtained by calcining the dried powder at 600 °C for 4 h. For the mixed metal oxide spinels, a modified co-precipitation method was used [32–34]. The molar ratio of the corresponding precursors (Zn:Mn, Co:Mn, and Zn:Co) was kept at 1:2. Then, a 0.1 M ammonium hydroxide solution was added to each set of bi-metallic precursor solutions with mild stirring until the pH was 9.0. The resulting precipitates were filtered, washed with water, dried at 100 °C for 8 h, and calcined at 600 °C for 4 h.

2.3. Catalytic glycolysis of PET

A stainless steel (SS 316) batch-type autoclave reactor (10 mL) was charged with 0.3 g of PET, a specified amount of EG (0.55–2.78 g, corresponding to EG/PET mole ratio of 5.7–28.7), and the desired amount of catalyst (0–0.006 g, corresponding to catalyst/PET weight ratio of 0.0–2.0 wt%). The air inside the reactor was

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