Recyclable Clay-Supported Heteropolyacid Catalysts for Complete Glycolysis and Aminolysis of Post-consumer PET Beverage Bottles

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Abstract
In this investigation, the use of phosphotungstic acid (PWA) and phosphomolybdic acid (PMA) as well as Zn\(^{2+}\)-containing kaolin and bentonite explored for chemical recycling of post-consumer poly(ethyleneterephthalate) (PET) wastes have been explored. The clay supported catalysts containing 5wt% of the metals and heteropolyacids (HPAs) synthesized using wet impregnation method. Nitrogen adsorption and desorption studies, SEM–EDX mapping, powder XRD, FTIR and XPS analysis have evaluated effect of metal ions and HPAs loading on the surface area, pore volume, elemental composition and crystalline nature. Total surface area of BET increased with a loading of 5 wt% of Zn\(^{2+}\), PWA and PMA on kaolin and bentonite, while the pore volume and pore diameter remain unchanged. SEM and EDAX mapping images showed that the heteropolyacids crystals are well dispersed on the surface and occupied interlayer spaces of the clay support. SEM–EDX showed that bentonite showed a better loading of PWA and PMA compared to kaolin. PET waste water bottles collected from the local market used for the chemical recycling process. The aminolysis reaction using Zn\(^{2+}\) and PWA loaded on bentonite showed complete depolymerisation of PET wastes to produce 87–98% of BHETA. The glycolysis reaction using the above catalysts showed complete depolymerisation at 180–210 °C and yielded 78–90% of BHET. When comparing the clay, bentonite performed well in terms of heteropolyacid loading and afforded a higher yield of BHET and BHETA because of higher loading of Zn and HPA, as supported by SEM–EDX and XPS. We also examined reusability of the catalysts for glycolysis.

Keywords Aminolysis · Depolymerization · Glycolysis · Heteropolyacids · PET wastes · Chemical recycling · Circular economy

Introduction
The chemical recycling process for post-consumer polyesters such as PET and PLA could contribute to the development of circular economy, in which the valorisation of polyesters through chemical depolymerization into value added monomers [1, 2]. PET waste recycling methods are classified into four fundamental techniques for implementing plastics recycling: primary (closed loop), secondary (mechanical), tertiary (chemical), and energy recovery (combustion) [3, 4]. Preferably, the PET recycling performed by two main approaches viz., mechanical recycling [5] and chemical recycling [6–8] in order to recover either pure polymer or terephthalic acid derivatives, respectively. The chemical recycling process, especially the depolymerization of PET waste, considered using heterogeneous catalysts as an economical and eco—friendly method of recycling plastic waste since depolymerized products reused to produce PET [9] or polyurethane foams for automotive applications [10].

Chemical recycling, glycolytic transesterification using ethylene glycol (EG) or diethylene glycol (DEG) or any other glycol of PET chains yields bis(hydroxy alkyl) terephthalate, it is a substrate for PET synthesis in monomer or oligomers [11]. Most PET glycolysis depolymerization widely studied in the presence of EG catalyzed by Zn\(^{2+}\) salts or any other acidic catalyst [12, 13], ionic liquids and deep eutectic solvents [14] or by using enzyme catalysts [15] and microorganisms such as Microbacterium*.

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oleivorans and Thermobifida fusca cutinase [16]. Likewise, the aminolysis reaction used for the efficient depolymerization of PET polymer into terephthalamide derivatives [17]. The depolymerisation of PET polymer using various amines, etc., allylamine, morpholine, hydrazine, and polyamines have investigated [18].

The heterogeneous catalyst for chemical transformation [19] of PET waste could be quickly and thoroughly depolymerized into its monomer bis(2-hydroxyl ethyl) terephthalate (BHET). In an eco-friendly approach, ash got from orange peel [20] and bamboo leaf fly ash catalyst [21] used as a catalyst for PET depolymerization that yields 79% and 83% of the recrystallized product, respectively. These catalysts are non-toxic, renewable, accessible, and inexpensive catalysts for glycolysis of post-consumer polyethylene terephthalate waste. In parallel, inorganic metal oxide-based catalysts have contributed to the glycolytic and aminolytic depolymerization of PET wastes. For example, the glycolysis of PET waste accomplished through Mg–Al–O@Fe3O4 nanoparticles [22]. The aminolytic depolymerisation of PET wastes achieved using hydrazine monohydrate, as a novel homogeneous catalyst and advantageous with respective to cost effectiveness and more reactive towards degradation of PET polymer. The reaction recorded a significantly higher yield of up to 84% within 2 h at 65 °C and the final product is terephthalic dihydrazide, a useful intermediate [23] and ethylene diamine as an aminolyting agent [24, 25]. Chemical recycling of PET waste is accomplished by ionic liquids, metal salts, enzymes, and hydroxalicates as catalysts [26].

Kaolin clays provide solid support because of their inherent acidity, excellent thermal stability, and attractive structural features, such as easily controlled structure morphology [27]. Therefore, acidified with kaolin with a large specific surface area widely used as a wonderful catalytic carrier for many organic transformations [28–30] and furfural converted into cyclopentenones [31]. Heteropolyacids like phosphomolybdic acid supported bentonite used for the biowaste into biofuel as a Bronsted acid catalyst [32]. Heteropoly acids are concentrated solid acids that have ubiquitous applications in various fields [33, 34] and value-added products from lignin [35]. The mixture of bentonite is montmorillonite (85%) and other contaminants etc. illite, quartz, chlorite, and calcite. Montmorillonite structure comprises three layers, an octahedral-shaped alumina layer in the middle surrounded by two layers of tetrahedral silica (SiO4) form. The octahedral and tetrahedral layers contain monovalent and bivalent cations such as Na+, Ca2+ and Mg2+. This arrangement leads to the creation of interior space and a charging interlayer [36]. Recently, more attention focused on heteropoly acids (HPAs) because of their many advantages, which are also known as eco-friendly and economically viable alternatives to conventional acid catalysts because of their Bronsted acidity, high proton mobility, relatively excellent and chemical stability [37, 38].

In our previous study, the effect of aluminium, zinc and iron containing kaolin and bentonite catalysts evaluated for the depolymerisation of PET polymer using glycolysis reported [39, 40]. Among them, Zn2+ loaded bentonite showed better results than kaolin analogue and other metals. From our observation and from reported literature, the acidity of the catalyst playing a key role in triggering the glycolysis reaction. Based on our investigation, presently, we have investigated depolymerisation of the post-consumer PET soft drink bottles collected from the local market using glycolysis and aminolysis process catalyzed by heteropolycids impregnated kaolin and bentonite catalysts and the same compared with Al3+, Zn2+ and phosphomolybdic and phosphotungstic acids and characterized using BET, XRD, FT-IR, XPS and SEM and the structures of depolymerized products, N1, N4 -bis(2-hydroxy ethyl)terephthalamide (BHETA) and bis(2-hydroxy ethyl)terephthalate (BHET) confirmed by 1H NMR, 13C NMR and mass spectra. Hence, in the present investigation, the glycolysis and aminolysis reaction using heterogenous catalysts, we could expect that reaction proceeds in clean and pure product could be obtained. Therefore, the 1H NMR, 13C NMR, FT-IR and mass spectra run for the crude product isolated from the reaction mixture. In view of the above claims, the process could be economically and environmentally sustainable.

**Experimental**

**Materials**

Clay supports and other reagents such as kaolin, bentonite, aluminum nitrate, zinc nitrate, phosphotungstic acid (PWA), and phosphomolybdic acid (PMA) were purchased from SRL, India and Loba, India and used without further purification. All the glasswares and quick-fits we employed in the experimental work were made up of corning/borosil glass. These glasswares were washed thoroughly and dried in a hot air oven before use.

**Wet Impregnation of Heteropolycids and Metal Ions into Clay Catalysts**

The metal ions or HPAs impregnated at 5 wt% loadings into kaolin and bentonite catalysts with respect to clay weight were prepared. In this method, for loading percentage of Zn2+, Al3+ ions and HPA for varied while the amount of clay was kept constant. It was produced by stirring 5wt% of
Zn\textsuperscript{2+} using Zn(NO\textsubscript{3})\textsubscript{2}, Al\textsuperscript{3+} using Al(NO\textsubscript{3})\textsubscript{3}, as a metal-ion source dissolved in 50 mL of distilled water containing 10 g of clay and the mixture stirred well at 100 °C for 12 h. The impregnated catalysts were isolated by filtration followed by washing with 2 × 50 mL of distilled water and then the clay catalysts dried in the oven at 90 °C for 6 h. The dried clay samples were kept in a desiccator during the study of this investigation.

Characterization of Clay Catalysts

The synthesized catalysts characterized by using XRD to determine crystalline nature of the catalysts, while the surface area and pore diameter of the catalysts were obtained from the nitrogen absorption and desorption analysis. The XRD analyzed performed on BRUKER D2 PHASER (XE-T Edition) using powder X-ray diffraction at 2θ angle between 10 and 80 and operating at 9.0 kW (CuKα radiation = 1.5406 Å). Nitrogen adsorption and desorption measurements were made on a volumetric gas adsorption apparatus (BELSORB MAX, Japan, Version: 1.3.12). The average pore diameter and average pore volumes were calculated using the adsorption branch of the N\textsubscript{2} isotherms based on the Barrett-Joyner-Halenda (BJH) model. The specific surface area of the catalysts was calculated using the BET equation. The Fourier transformed infrared spectra in the transmittance mode are reported in the range 400–4000/cm at room temperature using the KBr disc technique spectrometer (IRTracer-100, Shimadzu). The FT-IR spectra used to identify the presence of functional groups of the catalysts with respect to characteristic vibrational peaks. The morphology and elemental compositions were determined via SEM–EDX of the original clay and ion-exchanged clay materials received by the scanning electron microscope (SEM, JCM—7000 measurement data). The spin–orbit coupling using XPS (AXIS Ultra DLD, Shimadzu) measured binding energy.

Catalytic Activity

The catalytic activity of 5wt% of Zn\textsuperscript{2+}, Al\textsuperscript{3+}, PWA and PMA loaded kaolin and bentonite has been studied toward glycolysis and aminolysis of PET waste using ethylene glycol as glycolyte reagent and ethanolamine as aminolyte reagent under normal atmospheric conditions except reaction temperature (Scheme 1).

General Procedure for Glycolysis of PET Wastes using Ethylene Glycol

In the typical glycolysis reaction of PET wastes, 1 g of crushed PET chips was added to a 100 mL two neck flask containing 20 mL of preheated ethylene glycol medium (Preheated ethylene glycol at 130–150 °C for quick dissolution of PET chips). The mixtures were stirred well using a magnetic stirrer and heated to 180–210 °C. Temperature of the reaction system was maintained using a temperature controller. After reaching the optimal temperature, 50 mg of catalyst (5 wt% with respect to PET weight) was added. After 2 h time interval, 0.5 mL of reaction mixture was diluted by acetone and the reaction progress monitored using pre-coated aluminium TLC plates (E-Merck, UK, Silicagel G60 F254 indicator) containing 356 nm UV indicator. The spots were eluted using n-hexane and ethyl acetate (70:30) solvent mixture the spots were identified using a UV detector using a 356 nm light source. When the reaction is completed, the mixture was added to 100 mL of distilled water and then filtered through Whatman paper to remove the catalyst. In the case of glycolysis, we have identified issues associated with the isolation of the final product from water because the product is water soluble (Solubility is 17.61 g/L at 25 °C). However, the final product is obtained completely by extraction with chloroform and the final yield is calculated. The above procedure used for all the glycolysis reaction.

General Procedure for Aminolysis of PET Wastes using Ethanolamine

Similar to the glycolysis reaction, the aminolysis reaction is carried out using 1 g of crushed waste PET polymer chips was taken in 100 mL two-necked flask and to that 10 mL of ethanolamine was added (preheating of ethanolamine not necessary for the aminolysis reaction). The reaction is heated to 150–160 °C and maintained using a controller. After completion of the reaction, the mixture was diluted with water, and the catalyst was removed by simple filtration.
The reaction filtrate kept under 5 °C for 24 h and aminolyzed product obtained as light yellowish crystals. From the weight of the product, the yield is calculated with respect to the PET weight.

**Characterization of Depolymerized Products**

The depolymerized products BHET and BHETA were identified using 1H and 13C NMR spectra of the products obtained from glycolysis and aminolysis reactions respectively were recorded using CDCl3 as a solvent and TMS as an internal standard (Bruker Avance III operating at 500 MHz). In addition, the mass spectrum also recorded using (Shimadzu, LCMS-2020, ionization method: EI) and recorded the FT-IR spectrum using the KBr pellet technique (Shimadzu, IRTracer 100).

**Results and Discussion**

**Synthesis of Catalysts**

The commercially available kaolin and bentonite clay were purchased from Loba Chem Pvt. Ltd, India and used without further purification for the impregnation with Zn2+, and Al3+ nitrate salt and heteropolyacids were used. The wet impregnation method was successfully employed for the metal ions loading process [41]. The 5% weight load on the metal ions, however, a weight loss of 1–2% weight was observed when drying at 80 °C due to loss of moisture content in the clay sample. The synthesized catalysts were characterized by nitrogen adsorption and desorption, FTIR, powder X-ray diffraction (PXRD), SEM with EDX mapping, and XPS studies.

**BET Surface Area Analysis**

Pore volume, pore size distribution, and BET surface area are essential characteristics of porous material to act as a catalyst or catalyst support. The catalytic activity of clay material could be correlated with modification of surface area and pore volume before and after loading of metal ions (Al3+ and Zn2+) and heteropolyacids (PWA and PMA). The impact on porosity modification obtained from nitrogen adsorption–desorption studies. BET adsorption–desorption studies are extensions of Langmuir theory applied for multilayer adsorption on a homogeneous surface. The study is very helpful for finding gas–solid adsorption systems. The BET study is enabling the determination of the specific surface area of the catalysts. In addition to BET, the BJH model has been used to determine the average pore volume and pore diameter of porous materials. Since nitrogen gas is a non-reactive on acid or base surfaces, nitrogen adsorption–desorption isotherm used as a tool to build the BET and BJH model for the determination of surface area and pore details. In Fig. 1a, b, the results of the nitrogen adsorption and desorption isotherms of kaolin and bentonite impregnated with Zn2+, PWA, PMA and Al3+ compared to pure kaolin and bentonite, respectively. The average pore diameter calculated from the BJH model and the average pore distribution are given in supplementary information Fig. S1. The calculated BET surface area and average pore diameter and pore volume calculated using the BJH model are summarized in Table 1.

The typical adsorption and desorption of N2 gas with respect to relative pressure (P/Po) have been recorded. It is interesting to note that, Kaolin supported catalysts showed Type II adsorption isotherm (Fig. 1a) and bentonite supported catalysts showed Type IV adsorption pattern with clear Hysteresis loop (Fig. 1b). The type II and IV adsorption pattern indicates the presence of both macro- and mesoporou Nature of clay materials [42]. The formation of hysteresis loop indicates capillary condensation of gas molecules in the mesopores [43, 44]. In Fig. 1b, it is very interesting to note that pore widening is occurring while impregnation of 5wt% of PMA, PWA and Zn2+ on the bentonite support. On the other hand, the impregnation of metals and heteropoly acids did not show a significant effect on the porous nature of the kaolin support. The uptake of N2 occurring at relative pressure of 0.48–0.52 indicates micropore filling. Average pore size distribution in supported kaolin and bentonite catalysts showed in supplementary information Fig. S1. The average pore distribution showed the presence of the micro- and mesoporous nature of the clay materials. Impregnation with metals and heteropoly acids has a clear impact on surface area and pore size (Table 1).

In our previous studies on bentonite and kaolin clay using BET and BJH revealed that bentonite exhibits a surface area of 19.1 m2/g with a pore volume of 0.071 cm3/g and a pore diameter of 15.79 nm. Similarly, the kaolin clay showed a surface area of 5.1 m2/g with an average pore volume of 0.0200 cm3/g and a pore diameter of 17.36 nm. In the present study, the pure kaolin (Fig. 1a) showed BET surface area 6.602 m2/g with pore volume 0.0483 cm3/g and pore diameter 2.43 nm. However, it is interesting to note that ion exchange with Al3+, Zn2+, PWA and PMA showed notable changes in surface area and porosity, as discussed earlier (Table 1). The impregnation of 5 wt% loading of metal ions or heteropolyacids increased in surface area from 12.504, 16.309 and 19.449 m2/g, and pore volume increased from 0.0483, 0.0522 and 0.0605 cm3/g for Zn2+, Al3+ and PMA respectively. In contrast, pore diameter decreased from 2.43 to 2.14, 1.22 and 1.66 nm for ion exchanged kaolin catalysts. Similarly, the pure bentonite clay (Fig. 1b) showed BET surface area 14.533 m2/g with pore volume 0.0317 cm3/g and pore diameter
1.66 nm. Like the effect of loading on kaolin, the specific area, pore volume, and pore diameter of the bentonite catalysts increased (Table 1). For example, especially for PWA, Zn\(^{2+}\) and PMA an increase in surface area from 14.533 to 23.949 m\(^2\)/g, pore volume from 0.0317 to 0.0832 cm\(^3\)/g, respectively observed. As compared to pure kaolin and bentonite, 5wt% PMA kaolin and bentonite showed a tremendous increase in the surface area and pore volume and...
we observed marginal variation in surface area and porosity for Zn$^{2+}$, PWA and Al$^{3+}$-exchanged clay catalysts.

**XRD Pattern of Kaolin And Bentonite Catalysts**

The powder XRD patterns of pure kaolin and bentonite, as well as ion exchanged analogues, recorded at 2θ angles between 10° and 80°. The pure kaolin, bentonite and ion-exchanged catalysts presented in Fig. 1c, d. XRD analysis can determine mineralogical composition of the clay catalysts. To find the effect of impregnation on the crystalline nature, the diffraction pattern of a catalyst supported by 5% metal ions and HPA compared with pure kaolin and bentonite [44]. Bentonite is comprising 7–39, 0.4–21, 30–75, and 5–20% kaolinite, montmorillonite, quartz, and cristobalite respectively. However, the main crystalline phases of bentonite are montmorillonite and quartz. Bentonite forms lattice structures comprising a single plate between alumina and silica plates. Owing to the layer system, montmorillonite expand and contract upon impregnation with metal ions. On the other hand, the crystalline nature could be completely collapsed because of exceeding the loading capacity limit of impregnation. The loading of metal ions and heteropolyacids could be expected to occupy the inter-layer space of montmorillonite that can be reflected by the size of its intermediate space (d001 and d020) of montmorillonite [45]. The diffraction pattern of supported bentonite clay Zn$^{2+}$, PWA, PMA and Al$^{3+}$ catalysts was confirming a sharp peak at 2θ value of 29.10° at which they are responsible for the reflections of (001) plane of clay (Fig. 1d). The peak at 62.50° at 2θ the reflection by a (060) plane indicates well-crystallized kaolin. The diffraction peak at 19.25° and 25.10° was also observed in all samples, revealing the presence of a small amount of quartz along with kaolin catalysts [40, 47]. Since the diffraction patterns of 5 wt% of Zn$^{2+}$, PWA, PMA and Al$^{3+}$ loaded clay is almost similar to that of pure kaolin, it is assumed that the impregnation process does not make any significant impact on the crystalline nature of the clays. Similar XRD patterns also suggest that loading up to 5.0 wt% does not affect the crystalline nature of the catalyst. In addition, the retaining of porous nature of supported clay catalysts have been confirmed by N$_2$ adsorption and desorption studies.

**FT-IR Analysis of Supported Clay Catalysts**

FTIR spectra of raw kaolin and wet impregnation samples of 5 wt% Zn, PWA, PMA and Al-kaolin samples in the wave number range of 4000–400/cm shown in Fig. 1e (Whole FT-IR spectra given in the Supplementary information, Fig. S2). Infrared spectra of the kaolin absorption band at 820/cm and 860/cm attributed to Si–O–Al vibrations, and the band at 960/cm assigned to Al–OH bend vibration. The broad peak at 1060/cm corresponds to Si–O–Si in plane vibration and at 1130/cm allocated to asymmetric Si–O–Si stretching vibration. The band appears at 3700/cm, associated with the hydroxyl group consistent with the kaolin structure. The bands at 1058/cm and 900/cm correspond to the Si–O stretching vibration and OH bending mode of vibration, respectively [12]. The bands appearing at 460–532/cm correspond to Mg–O stretching vibration [49]. A broad band appears at 3424/cm, it is corresponding to OH asymmetric and symmetric stretching vibrations of M–OH, and a band at 1638/cm is similar to bending vibrations of d–OH. The band appears at 3700/cm, corresponding to the hydroxyl moiety of the bentonite layer [50]. The infrared spectrum of PWA/bentonite exhibits identical bands at 2800 and 2872/cm, which correspond to the
C–H stretching of the alkyl chain. The band appears at 1360/cm and corresponds to carbonyl moiety symmetric stretching vibrations. The existence of characteristic groups of Zn$^{2+}$, Al$^{3+}$, PWA, and PMA impregnated in kaolin and bentonite is very difficult to find out from FT-IR due to overlapping of peaks.

**SEM–EDX Mapping Analysis**

SEM analysis combined with EDX elemental mapping used to find elemental composition and the presence of impregnated catalytic sites in clay framework. Figures 2a–c and 3a–c summarises the impregnated kaolin and bentonite catalysts respectively analyzed by EDX analysis to find out the percentage of elemental composition (whole SEM–EDX images, elemental mapping for supported kaolin and bentonite catalyst given in Supplementary information, Figs. S4 and S5 respectively). Similarly, the estimated composition of supported kaolin and bentonite catalysts summarised in Tables 2 and 3, respectively. Figure 2a and Table S1 show the mass and atomic percentage of Zn$^{2+}$ in the Zn$^{2+}$ impregnated kaolin catalyst and the weight percent composition of Zn$^{2+}$ with respect to Al$^{3+}$ and Si$^{4+}$ is found to be 0.16 ± 0.03%. The EDX spectrum showed (Fig. 2a) showed presence of Zn$^{2+}$ and values of elemental mapping signifies that the impregnation of Zn$^{2+}$ is less. On other hand, according to Fig. 2b indicates EDX spectrum of PWA loaded kaolin catalyst. The wet impregnation of PWA in kaolin is found to be very significant and the% mass of W$^{6+}$ found to be 3.43 ± 0.10% when compared to Al$^{3+}$ and Si$^{4+}$ and theoretically, we have synthesized 5wt% of PWA containing kaolin with respect to the weight of W$^{6+}$ in PWA. The mass% of W$^{6+}$ is found to be close with theoretical % of W$^{6+}$. On the contrary, the composition of Mo$^{6+}$ from PMA loaded with kaolin showed 0.18 ± 0.02% of Mo$^{6+}$, which is found to be much lower compared to the theoretical value (Fig. 2c).

Apart from the elemental composition, SEM images evincing the surface morphology of the supported catalyst is similar to pure kaolin. There is no change in the morphology of the catalyst proves that phosphotungstic acid and phosphomolybdic acid species scattered well into
Fig. 3  a, b and c EDAX spectrum; d, e and f SEM images; g, h and i XPS spectra of Zn$^{2+}$, PWA and PMA supported bentonite catalysts

Table 2  SEM–EDX mapping mass percentage and atomic percentage of kaolin catalysts

| Elements | 5wt% Zn-Kaolin | 5wt% PWA-Kaolin | 5wt% PMA-Kaolin |
|----------|----------------|-----------------|-----------------|
|          | Mass (%)       | Atomic (%)      | Mass (%)        | Atomic (%)      | Mass (%)       | Atomic (%)      |
| O        | 59.43 ± 0.15   | 71.81 ± 0.19    | 54.40 ± 0.20    | 69.52 ± 0.26    | 53.93 ± 0.18   | 67.11 ± 0.23    |
| Na       | 0.11 ± 0.01    | 0.09 ± 0.01     | 0.31 ± 0.01     | 0.28 ± 0.01     | –              | –               |
| Al       | 13.65 ± 0.06   | 9.78 ± 0.04     | 16.85 ± 0.08    | 12.77 ± 0.06    | 15.15 ± 0.07   | 11.18 ± 0.05    |
| Si       | 26.39 ± 0.09   | 18.16 ± 0.06    | 19.55 ± 0.09    | 14.23 ± 0.07    | 30.33 ± 0.11   | 21.50 ± 0.08    |
| K        | 0.13 ± 0.01    | 0.07 ± 0.00     | 5.26 ± 0.06     | 2.75 ± 0.03     | 0.19 ± 0.01    | 0.09 ± 0.01     |
| Fe       | 0.14 ± 0.01    | 0.05 ± 0.01     | 0.21 ± 0.02     | 0.08 ± 0.01     | 0.23 ± 0.02    | 0.08 ± 0.01     |
| M*       | **0.16 ± 0.03** (Zn) | **0.05 ± 0.01** (Zn) | **3.43 ± 0.10** (W) | **0.38 ± 0.01** (W) | **0.18 ± 0.02** (Mo) | **0.04 ± 0.00** (Mo) |

Bold values indicate Metal ions and HPA loaded on Kaolin and Bentonite

*M—Metal loadings from Zn, W from PWA, and Mo from PMA
the hexagonal holes [48]. Further, it is confirmed by X-ray diffraction analysis and BET surface area analysis. Figure 3a is SEM–EDX analysis of Zn$^{2+}$ loaded bentonite support. EDX analysis revealed that the mass and elemental composition of Zn$^{2+}$ is 3.73 ± 0.16 and 1.18 ± 0.05% respectively (Table 3). It is interesting to note that the amount of Zn$^{2+}$ loading found higher when compared with kaolin supported analogue. We have followed, although under similar experimental conditions, the bentonite is showing excellent loading capacity, especially in supported clay catalysis. We have clearly seen that regarding catalytic activity towards depolymerization of post-consumer PET wastes using bentonite impregnated with Zn$^{2+}$ and Al$^{3+}$ performed excellently while comparing kaolin-supported analogues [39, 40]. The SEM–EDX spectrum of PWA loaded bentonite shown in Fig. 3b and Table 2, respectively. The SEM–EDX analysis confirmed the presence of W$^{6+}$ and the composition of PWA-bentonite showed 14.74 ± 0.12 wt% of W$^{6+}$ in bentonite clay. It strongly shows the successful impregnation of PWA in bentonite catalysts [51]. EDX analysis also revealed other elements present in bentonite clay, namely Na$^+$ in 2.01 ± 0.03, Mg$^{2+}$ in 1.13 ± 0.02, Al$^{3+}$ in 8.56 ± 0.05, Si$^{4+}$ in 19.12 ± 0.07, Ca$^{2+}$ in 1.60 ± 0.03 and Fe$^{2+/3+}$ in 4.90 ± 0.08% [36]. Figure 3c is the EDX spectrum of PMA loaded bentonite. We found the percentage of mass of Mo$^{6+}$ to be 1.06 ± 0.03%, while compared to the kaolin support, we found bentonite to be the best catalytic support with a higher metal ion loading capacity [51]. Comprehensive, the mass and atomic % values signify that amount of PWA and PMA loading on bentonite support is higher compared to PWA and PMA supported kaolin catalysts. FT-IR results in clear agreement with SEM–EDX studies, this indicates continued layer broadening of bentonite. In addition, the BET surface area analysis showed increasing surface area of bentonite and kaolin support upon PMA and PWA loading. The higher loading capacity of bentonite resulted in higher catalytic activity, which eventually afforded excellent yield of a pure glycolyzed and aminolyzed single product, BHET and BHETA.

EDX analysis of pure bentonite showed that the presence of O, Na, Mg, Al, Si, Ti, Fe and similar components have been present in 5wt% of impregnated bentonite catalysts with Zn$^{2+}$, PWA and PMA and SEM images along with elemental mapping and EADX spectrum given in Fig. 3a–c respectively [52]. We summarize the mass and elemental composition of impregnated bentonite catalysts in the supplementary information Table 3.

### Table 3 SEM–EDX mapping mass percentage and atomic percentage of bentonite catalysts

| Elements | 5wt% Zn-bentonite | 5wt% PWA-bentonite | 5wt% PMA-bentonite |
|----------|-------------------|-------------------|-------------------|
|          | Mass (%) | Atomic (%)       | Mass (%) | Atomic (%)      | Mass (%) | Atomic (%)               |
| O        | 51.69 ± 0.19 | 67.08 ± 0.25      | 47.33 ± 0.15 | 68.57 ± 0.21     | 54.38 ± 0.15 | 69.05 ± 0.19         |
| Na       | 2.38 ± 0.04  | 2.15 ± 0.04       | 2.01 ± 0.03  | 2.03 ± 0.03       | 3.06 ± 0.04  | 2.70 ± 0.03          |
| Mg       | 2.52 ± 0.04  | 2.15 ± 0.03       | 1.13 ± 0.02  | 1.07 ± 0.02       | 1.45 ± 0.02  | 1.21 ± 0.02          |
| Al       | 10.62 ± 0.07 | 8.18 ± 0.05       | 8.56 ± 0.05  | 7.36 ± 0.04       | 9.70 ± 0.05  | 7.30 ± 0.04          |
| Si       | 22.00 ± 0.10 | 16.26 ± 0.08      | 19.12 ± 0.07 | 15.78 ± 0.06      | 22.61 ± 0.08 | 16.35 ± 0.06         |
| K        | 2.14 ± 0.04  | 1.14 ± 0.02       | 0.48 ± 0.01  | 0.28 ± 0.01       | 0.45 ± 0.01  | 0.24 ± 0.01          |
| Fe       | 4.45 ± 0.10  | 1.65 ± 0.04       | 4.90 ± 0.08  | 2.03 ± 0.03       | 5.39 ± 0.08  | 1.96 ± 0.03          |
| M$^*$    | 3.73 ± 0.16 (Zn) | 1.18 ± 0.05 (Zn) | 14.74 ± 0.12 (W) | 1.86 ± 0.02 (W) | 1.06 ± 0.03 (Mo) | 0.22 ± 0.01 (Mo) |

Bold values indicate Metal ions and HPA loaded on Kaolin and Bentonite

*M—Metal loadings from Zn, W from PWA, and Mo from PMA

### Morphology Analysis of Supported Catalysts

The SEM images (Supplementary information, Fig. S6) and Fig. 2d–f show the surface morphologies of the kaolin before and after wet impregnation of Zn$^{2+}$, PWA and PMA, respectively. SEM images revealed that no notable modifications in the morphology of pure kaolin (Fig. S6) and ion-exchanged metal ions (Fig. 2d, e, f) have been observed. However, at a closer look at higher magnification (7000 ×, 2 µM) the layered structure of clay can clearly seen in Fig. 2d–f. The clear appearance of layered structure could be because of broadening of inter layer distance because of impregnation of PMA and PWA, which is higher molecular size [53]. Similarly, the SEM images of pure bentonite and Al$^{3+}$ impregnated bentonite (Supplementary information, Fig. S7) and Zn$^{2+}$, PWA, PMA, and Al$^{3+}$ loaded bentonite are illustrated in Fig. 3d–f, respectively. The SEM images revealed the morphology of bentonite consist of stacked layered structure [51, 53]. Due to the layered structure, the SEM imaging showed the effects of impregnation on clay supports. In pure bentonite clay (Fig. S7a), the layered nature of clay is not clearly visible even at higher magnification (3000 ×, 5 µM). Whereas Figs. 3d and S7b are Zn$^{2+}$ and Al$^{3+}$ incorporated bentonite showed rough surface and deformed layered structure. However, the XRD studies confirmed that the
crystalline nature of bentonite is retained even after metal ion loading. More interestingly, the PWA loaded bentonite showed small crystallite PWA crystals deposited on the surface (Fig. 3e). The resulting surface morphology of the PWA/bentonite catalyst is completely different from that of pure bentonite. The SEM images clearly showed that PMA is homogeneously dispersed on the surface of the bentonite (Fig. 3f).

XPS-Analysis and Elemental Composition

The chemical composition of Zn$^{2+}$, Al$^{3+}$ and HPA loaded kaolin and bentonite was recorded by X-ray photoelectron spectroscopy (XPS). The XPS spectra of Kaolin and bentonite supported Zn$^{2+}$, PWA and PMA catalysts are shown in Figs. 2g–i, 3g–i, and binding energy (eV), metal to Al$^{3+}$ ratio and atomic composition is summarised in Tables 4 and 5, respectively. Figures 2g and 3g are the XPS spectra of Zn$^{2+}$ loaded kaolin and bentonite, respectively. Zn$^{2+}$ loaded kaolin as well as bentonite support showed two peaks at 1022 and 1045 eV are the binding energies of Zn$^{2p3/2}$ and Zn$^{2p1/2}$, which is related to the spin–orbit splitting of about approximately 22 eV. The metal-to-Al$^{3+}$ ratio of bentonite showed a higher content of Zn$^{2+}$ loading compared to catalysts supported by kaolin. Due to this higher loading capacity, the bentonite supported catalysts showed higher catalytic activity towards depolymerisation of PET wastes in glycolysis and aminolysis reaction. All XPS spectra showed a symmetric peak approximately at 533 eV that was O$_2^-$ connected to Si and attributed to SiO$_2$ based materials and summarized in the Supplementary Material, Figs. S8–S19.

Table 4  Binding energies values (eV) for Zn$^{2+}$, W$^{6+}$ of PWA, Mo$^{6+}$ of PMA and Al-Kaolin spectra and surface M/Al compositions of samples and reference ZnO, PWA and PMA

| Catalysts | Metals | Binding energy (eV) | M/Al ratio (surface) | Atomic (%) |
|-----------|--------|---------------------|----------------------|------------|
| Zn-kaolin | Zn$^{2p3/2}$ | 1022.12 | 0.1854 | 2.07 |
|           | Zn$^{2p1/2}$ | 1045.16 | 0.0618 | 0.69 |
|           | Al 2p B | 75.75 | – | 7.02 |
|           | Al 2p A | 74.72 | – | 4.14 |
| PWA-kaolin | W 4f$^{7/2}$ | 36.06 | 0.0055 | 0.07 |
|           | W 4f$^{5/2}$ | 38.19 | 0.0039 | 0.05 |
|           | Al 2p B | 75.51 | – | 7.93 |
|           | Al 2p A | 74.63 | – | 4.65 |
| PMA-kaolin | Mo 3d$^{3/2}$ | 232.74 | 0.0033 | 0.04 |
|           | Mo 3d$^{5/2}$ | 235.73 | 0.0016 | 0.02 |
|           | Al 2p B | 75.62 | – | 7.69 |
|           | Al 2p A | 74.79 | – | 4.36 |
| Al-kaolin | Al 2p B | 75.42 | 0.2555 | 3.09 |
|           | Al 2p A | 74.52 | 0.1264 | 1.53 |
| Pure kaolin | Al 2p B | 75.64 | – | 9.19 |
|           | Al 2p A | 74.65 | – | 2.91 |

Table 5  Binding energies values (eV) for Zn$^{2+}$, W$^{6+}$ of PWA, Mo$^{6+}$ of PMA and Al-bentonite spectra and surface M/Al compositions of samples

| Catalysts | Metals | Binding energy (eV) | M/Al ratio (surface) | Atomic (%) |
|-----------|--------|---------------------|----------------------|------------|
| Zn-bentonite | Zn$^{2p3/2}$ | 1022.99 | 0.3161 | 2.07 |
|           | Zn$^{2p1/2}$ | 1045.10 | 0.1053 | 0.69 |
|           | Al 2p A | 74.69 | – | 8.73 |
| PWA-bentonite | W 4f$^{7/2}$ | 35.62 | 0.0129 | 0.11 |
|           | W 4f$^{5/2}$ | 37.82 | 0.0094 | 0.08 |
|           | Al 2p B | 75.15 | – | 6.99 |
|           | Al 2p A | 74.54 | – | 1.52 |
| PMA-bentonite | Mo 3d$^{3/2}$ | 231.97 | 0.0156 | 0.13 |
|           | Mo 3d$^{5/2}$ | 235.08 | 0.0016 | 0.09 |
|           | Al 2p A | 74.59 | – | 8.3 |
| Al-bentonite | Al 2p B | 75.31 | 1.19 | 9 |
|           | Al 2p A | 74.65 | – | 7.55 |

Figures S13b and S19b showed binding energy peaks of Al$^{3+}$ in Zn$^{2+}$ loaded kaolin and bentonite. XPS analysis revealed the presence of binding energies of 2pA and 2pB for Al$^{3+}$ approximately at 74.72 and 75.75 eV in kaolin and bentonite-supported catalysts. Figures 2h and 3h are the peaks of W$^{6+}$ binding energy in phosphotungstic acid (PWA). The presence of W$^{6+}$ in PWA supported on kaolin and bentonite is confirmed by the binding energy peaks at 36.06 and 38.19 eV attributed to spin–orbit coupling 4f$_{7/2}$ and 4f$_{5/2}$ states. The mineral composition of W$^{6+}$ to Al$^{3+}$ is found to be 0.07 (7%) and 0.11 (11%) with respect to Al$^{3+}$ for kaolin and bentonite loaded with PWA, respectively. Thus, the presence of a higher loading of PWA in bentonite was attributed to the higher catalytic activity. In the case of, kaolin and bentonite loaded with phosphomolybdic acid (PMA) showed Mo$^{6+}$ spin orbit coupling binding energy peaks approximately at 233 and 236 eV, which is attributed to transition states 4d$_{5/2}$ and 4d$_{3/2}$ (Figs. 2i, 3i). Similarly, bentonite showed higher phosphomolybdic acid (PMA) loading is observed from the elemental composition of Mo$^{6+}$, which is estimated to be 0.04 (4%) and 0.13 (13%) for PMA loaded kaolin and bentonite respectively.

Figure S13e and S13f is spin–orbit coupling peaks of Al$^{3+}$ in Al$^{3+}$ loaded kaolin and bentonite respectively. The binding energy peaks at 75.50 and 74.60 eV, which corresponds to Al 2pB and Al 2pA. Similarly, pure kaolin and bentonite showed binding energies of Al$^{3+}$ at 75.60 and 74.60 eV, which corresponds to the spin–orbit coupling states of Al 2pB and Al 2pA.
Depolymerisation of PET Waste using Glycolysis and Aminolysis

Glycolysis and aminolysis are the common depolymerisation reaction applied for PET wastes. The presence of ester linkage in the PET polymer chain enables the hydrolysis using acids or bases to give terephthalic acid. However, the ester linkage could be cleaved using methanol to give dimethylterephthalate (DMT) as the final product through the transesterification reaction. However, the methanolysis process needs a high-pressure reactor to overcome the pressure built by a low-boiling methanol solvent. By using a similar transesterification methodology, ethylene glycol or ethanolamine has been used to depolymerise PET waste to generate bis(2-hydroxyethylene)terephthalate (BHET) or bis (2-hydroxyethylene) terephthalamide (BHETA), respectively. However, a Lewis or Bronsted acid catalyst required to activate the ester carbonyl group and trigger the transesterification reaction and higher reaction temperature is required for the dissolution of PET chips in ethylene glycol for the complete depolymerisation of PET.

Thus, in the present investigation, an economical catalyst support, clay material has been opted to prepare Lewis and Bronsted acid supported catalyst. Ethylene glycol and ethanolamine has been used as a glycolyting/aminolyting agent as well as solvent. The depolymerisation reaction has been carried out in the presence of 10wt% of the clay catalyst.

In both cases, Fig. 4a, b, the glycolysis and aminolysis of PET waste using kaolin and bentonite clay loaded with Zn²⁺, PWA and PMA, respectively. The use of ethylene glycol (EG) and ethanol amine (EA) as a common depolymerizing agent for glycolysis and aminolysis process. The glycolytic depolymerisation lead to monomer, bis(hydroxyethyl)terephthalate (BHET) and aminolytic depolymerisation lead to monomer, bis(hydroxyethyl)terephthalamide (BHETA). In both depolymerisation reactions, we have observed complete depolymerisation of PET wastes. The final product isolated from the reaction mixture is highly pure is confirmed by ¹H and ¹³C NMR, in which the peaks correspond to PET

![Fig. 4](image-url)

**Fig. 4** a Glycolysis of PET wastes; b Aminolysis of PET wastes using Al³⁺, Zn²⁺, PWA and PMA on kaolin (K) and bentonite (B); c Catalysts recycling studies using PWA and Zn²⁺ loaded kaolin (K) and bentonite (B)
The reaction time is 6–7 h for glycolysis, whereas the aminolysis required only 4–5 h for the complete depolymerisation. The reaction was monitored by TLC using an ethyl acetate to hexane ratio at 20:80. After completion of the reaction, the reaction mixture was diluted with hot water (100 mL) and filtered to the catalyst. After filtration, the reaction mixture was heated to 60 °C for 15 min and kept at 5 °C for 24 h for the glycolysis reaction and after heating the reaction mixture kept room temperature for 24 h for the aminolysis reaction mixture. In the case of aminolysis, the final product BHETA is obtained as colourless needle crystals from the reaction mixture at room temperature itself. Whereas the glycolyzed product, BHETA obtained by extraction using chloroform. In both the cases, the catalyst is removed by filtration after the reaction and washed with hot water (25 mL), dried at 110 °C for 6 h and used for next reaction cycle. We have tried with many diamines for aminolysis, ethanol amine is worked better at low temperature and afforded excellent yield of BHETA. However, the investigation on aminolysis of PET using different kinds of amine is proceeding in our laboratory. The crystals of BHETA filtered, dried and yield of the reaction calculated. Both 1H and 13C NMR, and mass spectral analysis showed BHETA is a single pure product.

Figure 4a, b are the result of the glycolysis and aminolysis reaction. In the case of glycolytic depolymerization reactions, Zn2+ and PWA loaded bentonite-supported clay catalysts gave 92 and 93% of BHET, respectively, when compared with kaolin-supported analogues. Whereas, Al3+ and PMA loaded bentonite catalyst showed 83% and 90% yield of BHET. On other hand, the aminolytic depolymerisation reaction revealed that Zn2+ and PWA loaded bentonite afforded 94 and 96% of BHETA respectively in comparison with kaolin supported analogues. Similarly, the glycolysis reaction was performed with ethylene glycol as the transesterification catalyst. In both reactions, the bentonite clay support found to be the better catalytic support as it is supported by BET surface area analysis, SEM–EDX, and XPS analysis. Bentonite support exhibited higher surface area as well as higher loading capacity of metal ions and HPA.

**Catalysts Recycling Studies**

The PWA and Zn2+ loaded kaolin and bentonite catalysts were subjected to recycling studies using glycolysis as a model reaction. At the end of each reaction cycle, the spent catalysts were filtered following washed with water and dried in the oven before the next reaction cycle. The yield of the depolymerized product obtained from the subsequent reaction cycle was compared (Fig. 4c). The study revealed that the catalyst can be reusable up to six cycles with marginal loss in yield. Among the catalysts, PWA and Zn2+ loaded bentonite catalysts showed better results. Higher catalytic activity of bentonite catalyst could be correlated with higher surface area of bentonite, which eventually can take more PWA and Zn2+ as supported by BET, SEM -EDX and XPS studies. The slower leaching of PWA from the surface and interlayer spaces is reflected in the yield of the BHET formed.

**Spectral Analysis of Depolymerised Products**

All depolymerized products would have been characterized by 1H, 13C NMR, and mass spectroscopy to confirm the structure. The chemical structure of BHET and BHETA is shown below and assignment of 1H and 13C NMR is summarised in the Table 6.

**1H NMR Spectrum**

The four aromatic (C3, C4, C6 and C7) hydrogens present in BHET have appeared (Supplementary information, Fig. S20) as singlets 8.08 ppm confirm the formation of the glycolyzed product, the BHET monomer. The 1HNMR run for the crude product showed singlet aromatic protons that confirmed the complete depolymerization of PET wastes [54]. In the case of BHET, the two hydrogens attach to carbon (C2 and C11) next to the ester carbonyl (C9 and C10) oxygen appeared as a triplet at 3.96 ppm. Another two hydrogens attached to carbon (C1 and C12) next to OH has appeared as triplet at 3.70 ppm. The former appeared downfield due to the presence of electron-withdrawing carbonyl oxygen attached. The OH proton appears as a broad singlet at 4.47 ppm due to the exchangeable nature of its kind. The deuterated CDCl3 solvent appeared as singlet 7.26 ppm [39, 40, 55]. Similarly, the 1H NMR of the crude depolymerized product obtained from the aminolysis of PET using 2-amino ethanol is given in the supplementary information (Fig. S21). The main aminolyzed product N1,N4-bis(2-hydroxyethyl)terephthalamide (BHETA) is a symmetrical molecule. Hence, the four aromatic (C3, C4, C6 and C7) hydrogens present in the central aromatic ring of BHETA were appeared as singlet 8.07 ppm confirming the formation of aminolysed product BHETA and complete depolymerisation of PET wastes. The two N–H protons of the amide linkage attached to the methylene group are observed as a triplet at 8.74 ppm and the –OH protons of the alcoholic group are observed at 2.64–2.65 ppm as a triplet [56]. In the case of BHETA, the two hydrogens attach to carbon (C2 and C11) next to amide carbonyl (C9 and C10) oxygen, and –NH appeared as a triplet at 3.48–3.51 ppm. Another two hydrogens attached to carbon (C1 and C12) next to OH has appeared as a triplet at 3.65–3.68 ppm. Therefore, presence of –N–H and –O–H protons confirms the 2-amino ethanol attached to terephthaloyl group to form the BHETA.
13C NMR Spectrum

13C NMR spectrum of BHET is shown in supplementary information (Fig. S22). The ester carbonyl carbon (C9 and C10) of BHET appeared at 166.16 ppm is showing single ester carbonyl present the structure and no other carbonyl carbons were recorded, which confirmed the presence of BHET as a single product. Since BHET is a symmetrical molecule, here are two aromatic carbons that appeared at 133.80 and 129.70 ppm. The peak at 134.0 ppm corresponds to C5 and C8 attached to ester carbonyl, and another peak at 129.70 ppm corresponds to C3, C4, C6 and C7 attached with hydrogen appeared as singlet with high intensity. The –CH2– carbons of the aliphatic chain (C2 and C11) attached to the ester carbonyl oxygen appeared at 67.0 ppm for BHET. The variation in –CH2– the shift is owing to two –CH2– attached to the chain. Hydroxyl group attached –CH2– carbons (C1 and C12) appeared at BHET at 61.10 ppm, respectively [39, 40], and we were not able to account for the peak appeared at 63.70 ppm [57]. The 13C NMR spectrum of the aminolysed product, BHETA is shown in the supplementary information (Fig. S23). The amide carbonyl carbon (C9 and C10) of BHETA appeared at 166.10 ppm, showing that the amide carbonyl has the structure that confirmed the symmetrical nature of the BHETA single product. Since, BHETA is a symmetrical molecule, there are two aromatic carbons that appeared at 137.10 and 127.60 ppm. The peak at 137.10 ppm corresponds to C5 and C8 attached to amide carbonyl, and another peak at 127.60 ppm corresponds to C3, C4, C6 and C7 attached with hydrogen appeared as singlet with high intensity. Two –CH2– carbons (C2 and C11) of the aliphatic chain attached to amide –NH– appeared at 42.7 ppm for BHETA. The second hydroxyl group connected to carbon (C1 and C12) –CH2– appeared at 60.1 ppm of BHETA [24].

Additionally, functional groups such as hydroxy and amide or ester carbonyl groups present in BHET (Fig. S24) and BHETA (Fig. S25) were analyzed through FT-IR [58]. In addition, the molecular weight of BHETA confirmed by the ESI–MS of the aminolysed product (Fig. S26). The mass spectrum showed a molecular ion peak at m/z 253.15 that indicated the molecular weight of BHETA. The peak at m/z 275.1 could be due to electron spray ionization of BHET by Na+ [24, 57].
Scheme 2  Proposed mechanism for glycolysis and aminolysis (X=O, NH)
Proposed Mechanism for Depolymerisation of PET Wastes

The depolymerisation of PET wastes occurring through cleavage of ester linkages by transesterification and transamidation reaction for glycolysis and aminolysis, respectively. The proposed mechanism of glycolysis and aminolysis catalysed by Lewis acids and polyoxometallates have discussed previously [14, 58–63]. In our present investigation, the transesterification and transamidation reaction of PET accomplished using glycols and amino alcohols, respectively. Both the reactions were promoted by Bronsted or Lewis acidic catalyst by activating the ester carbonyl oxygen [14, 55, 58–63] (Scheme 2). The glycolysis or aminolysis process initiated by accepting a lone pair of electrons on ester carbonyl oxygen by Lewis acidic sites such as Zn2+ or polyoxotungstate of HPA (I) [64]. Further, the activation of ester carbonyl oxygen led to promote carbonyl carbon electron deficient center. Parallely, the alcoholic oxygen of glycolysis or amino group of ethanol amine activated by taking the proton to form nucleophile (II) [64]. Subsequently, the electron deficient carbon undergoes electrophilic attack (III) by hydroxy group of ethylene glycol for glycolytic depolymerisation to give intermediate (IV). Similarly, the amino group of 2-aminoethanol attacks the carbonyl carbon for aminolysis. Finally, the intermediate (IV) undergo elimination of alcohol to give depolymerized PET. In the case of HPA supported clay catalysts, they act as Bronsted acid catalysts. It is well known that Bronsted acid sites activate the carbonyl, alcoholic, and amino group by protonating them [64]. Catalytic activity of the heteropolyacids enhanced by stabilization of the intermediates of PET polymer and ethylene glycol or ethanol amine [65, 66]. The use of porous bentonite and kaolin clay supports promote the catalytic activity of HPA by absorbing them on the porous surface. In the present investigation, HPA supported catalysts act as both Lewis and Bronsted acidic catalysts.

Conclusions

The present investigation on the depolymerisation of polyethylene terephthalate wastes have been effectively achieved by Lewis acidic (Zn2+ and Al3+) and heteropolyacids (PWA and PMA) supported kaolin and bentonite catalysts using glycolysis and aminolysis reaction at 150–210 °C. The kaolin and bentonite supported catalysts synthesised by the wet-impregnation method at 5wt% of Zn2+, Al3+, PWA and PMA. The crystallinity and structural morphology of the supported catalysts are analysed by X-ray diffraction and SEM. The elemental composition of the catalysts was estimated by using SEM–EDX mapping and XPS analysis. As shown by BET analysis, the surface area of the supported clay catalysts increased due to occupying of HPA and metal ions in the layered structure of clay. The heteropolyacids loaded catalysts showed better catalytic activity towards glycolytic and aminolytic depolymerisation of PET wastes when compared with Zn2+ and Al3+ supported catalysts. In comparison to PMA, PWA-supported catalysts showed better performance in depolymerisation of PET wastes. With respect to clay supports, bentonite was found to be the best support for HPA and metal ion loading when compared with kaolin support. The depolymerisation products, bis(2-hydroxyethyl) terephthalate and bis(2-hydroxyethyl) terephthalamide, are formed in the metal ion or HPA loaded catalysts on top of pure kaolin and bentonite. The chemical structure of BHET, BHETA is confirmed with 1H and 13C NMR, FT-IR and MS. Currently, the investigation of glycolysis and aminolysis of waste polyester fabrics using various glycols and aminoalcohols catalyzed by HPA-loaded catalysts and doped ZnO nano particles is under progress in our laboratory.

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Author Contributions GJ—Executed laboratory experiments and writing the manuscript, EG, AAHT, YI—Characterisation of catalysts, RD—Executed laboratory experiments, VS—Conceptualization, research planning, and manuscript drafting and submission.

Samples Samples of catalysts and depolymerized products are available from the corresponding author.

Declarations Conflict of interest The authors have declared that there is no conflict of interest.

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