Zn- and Ti-Modified Hydrotalcites for Transesterification of Dimethyl Terephthalate with Ethylene Glycol: Effect of the Metal Oxide and Catalyst Synthesis Method

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ABSTRACT: The activity and selectivity of hydrotalcites (HTs) can be suitably enhanced by the addition of different metal oxides. Zinc and titanium are prospective candidates for such a modification. Transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) using basic catalysts is an industrially important process for the production of bis(2-hydroxyethyl)terephthalate (BHET). BHET is a precursor for polyethylene terephthalate (PET) which is used in production of films, fibers, and molding materials. As against use of polluting liquid bases, solid bases could be employed. In the current work, transesterification of DMT with EG was studied over modified HT base catalysts wherein the HT was activated with the addition of zinc and titanium. These catalysts were prepared by the combustion synthesis using different fuels. The modified HT using Zn and Ti were well characterized by scanning electron microscopy, energy-dispersive X-ray spectrometry, Brunauer–Emmett–Teller surface area analyzer, temperature-programmed desorption, and X-ray diffraction. Effects of several parameters on the rate of reaction and conversion of the limiting reagent were investigated. Zinc-modified HT using glycine as fuel (Zn-HT-glycine) was found to be the most selective, active, and reusable catalyst. The Langmuir–Hinshelwood–Hougen–Watson model was used to establish the reaction mechanism and kinetics. All species were weakly adsorbed leading to a second-order kinetics. Using a mole ratio of 1:2 of DMT to EG and 0.05 g/cm³ Zn-HT-glycine loading resulted in to 64.1% conversion of DMT and 96.1% selectivity to BHET in 4 h at 180 °C. The apparent activation energy was 9.64 kcal/mol. The catalyst was robust and reusable.

1. INTRODUCTION

The green chemistry principles basically aim at waste reduction using atom economical safer processes, catalysis, and renewable resources.1 Catalysis is pivotal in developing economical and energy efficient processes and many organic transformations could be revisited from this angle.2 Heterogeneous catalysis is inherently superior to homogeneous catalysis and offers process intensification, easier catalyst separation, and less impact on the environment, reduces waste, and improves process economics.3 Many traditional bulk and fine chemical manufacturing facilities involve use of homogeneous bases which ought to be replaced by solid bases. Among all, hydrotalcites (HTs) and their modified structures have made great inroads in base catalyzed condensation reactions which cover aldol, cross-aldol, Claisen–Schmidt, and Knoevenagel condensations and also other reactions such as isomerization, alkylation, and hydrolysis reactions.4–6

Transesterification between dimethyl terephthalate (DMT) with ethylene glycol (EG) is a relevant process used for the production of bis(2-hydroxyethyl)terephthalate (BHET) which is a monomer for making polyethylene terephthalate (PET).7–9 PET is the fastest growing thermoplastic polymer which is used in the form of films, bottles, molding and fibers and increasingly in blends, composites, and nanocomposites.10,11

Transesterification is commonly catalyzed by acid or base catalysts12 and also by enzymes.14 Many catalysts such as Zn, Mn, Mg, and lead acetates7 are commonly employed for the

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transesterification between DMT and EG.\textsuperscript{13} In this reaction, a considerable amount of byproducts such as methyl 2-hydroxy-ethyterephthalate and methanol are formed along with BHET.\textsuperscript{7,14,15} The catalysts are homogeneous and nonreusable bases. In general, the esterification and transesterification reactions of carboxylic acids or esters with alcohols have been carried out over homogeneous catalysts such as mineral acids, metal hydroxides, and metal alkoxides. The replacement of these catalysts by solid catalysts enjoys various advantages, as was stated before.\textsuperscript{6,15} The effect of different homogeneous catalysts such as acetates of Pb, Co, Mg, and Mn and of the mixtures of Mg, Mn, and Zn acetates has been also studied.\textsuperscript{7,15,16} The reaction requires higher concentration of raw materials and catalyst which subsequently necessitates neutralization of the reaction mass and effluent treatment. Synthesis of poly(ethylene terephthalate) (PET) by transesterification of DMT with EG was performed in the presence of a few well-known catalysts including various lanthanide compounds.\textsuperscript{7,9} Mihail et al.\textsuperscript{16} suggested the reaction order of transesterification of DMT and EG being fractional over zinc oxide in the concentration range of 0.14–0.28%. Sorokin and Chebotareva\textsuperscript{17} reported that the reaction was first order with respect to EG over Zn stearate. However, it is reported that the transesterification reaction was first order in each DMT, EG, and homogeneous catalyst concentration, making it overall a third-order reaction.\textsuperscript{18} Besnoin et al.\textsuperscript{7} dealt with semi-batch melt transesterification of DMT with EG using zinc acetate as a catalyst. However, all above catalysts gave less selectivity toward BHET, requiring large catalyst/reactant ratio and nongreen solvents. Serio et al.\textsuperscript{19} have prepared a basic heterogeneous catalyst for transesterification of DMT with EG. Three different catalysts such as Al\textsubscript{2}O\textsubscript{3}, MgO, and calcined HT of Al–Mg with varying combination of both metals were investigated for transesterification and successive polycondensation to get poly(ethylene terephthalate) (PET) at 180 °C.

Transesterification reactions can be effectively conducted using HT which could be modified to render better activity and selectivity. Synthesis of HTs can be achieved using coprecipitation,\textsuperscript{20} sol–gel,\textsuperscript{21} template-assisted synthesis,\textsuperscript{22} decomposition of nitrates,\textsuperscript{23} and so forth. Such procedures intrinsically contain a number of steps to get the final catalyst making them lengthy and cumbersome, as well as they need a lot of process water. Therefore, different protocols have been suggested in the literature for synthesizing metal oxide(s) like HTs. Among them, combustion synthesis is a powerful alternative for making materials which not only render reproducible results but also involve reduced number of steps. Combustion synthesis gives fine nanoscale metal oxides depending on the source of fuel and ignition temperature. It can produce metal oxides with high surface area, pore volume, and mesoporosity, and therefore, it is one of the best methods to synthesize different catalysts.\textsuperscript{24,25} Combustion synthesis needs a fewer steps to make porous materials with controllable pore radii and particle size according to application.\textsuperscript{24} In the current work, the combustion synthesis method was adopted to prepare Ti- and Zn-modified HTs by using glycine and glycerol as fuel which is one of the novel aspects of the current work. Previously, Ti- and Zn-modified HTs were prepared by coprecipitation method and characterized by different high-end characterization techniques. Velu et al.\textsuperscript{26} have developed a novel series of HT like anionic clays containing Z\textsuperscript{4+} by a simple coprecipitation method. Further rehydration behavior of Mg\textsuperscript{2+}, Al\textsuperscript{3+} and Ti\textsuperscript{3+} containing layered double hydroxides (LDH) were studied by Das and Samal.\textsuperscript{27} Selective catalytic reduction of NO with ammonia was performed over Cu, Co, and Mn containing HTs.\textsuperscript{28} In all these reports, the method of preparation of modified HT is coprecipitation. The present work deals with a comparative study of Zn- and Ti-modified HTs synthesized by using the combustion method with two different fuels, namely, glycine and glycerol. Thus, the prepared catalysts were used for the first time to study the transesterification of DMT with EG in a solvent-free condition, which has resulted into better selectivity for BHET. A thorough investigation of catalyst synthesis and characterization was undertaken, along with the reaction mechanism and kinetic model. The current reaction is carried out with novel and cost-effective zinc-modified HT base catalyst to achieve good selectivity for the desired BHET with minimum quantities of starting materials employing solvent-free condition to make the process green.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. Among all of the catalysts, Zn–HT–glycine was the best for the reaction, and hence its complete characterization was done. It is recently published elsewhere\textsuperscript{29–31} (Supporting Information). Only a brief description is provided here.

2.1.1. Scanning Electron Microscopy and Energy-Dispersive X-ray Spectrometry. Scanning electron microscopy (SEM) images of Zn–HT–glycine at 1500, 2500, and 5000 amplification are shown in Figure 1a–c, respectively. The average particle size is in the range of 50–100 μm. It shows uneven particles, which are relatively uniform in size. It is generally seen for materials synthesized by the combustion method.

Energy-dispersive X-ray spectrometry (EDXS) was used to determine the whole composition of titanium, zinc, aluminum, and magnesium for all catalysts (Table 1). The ratio of composition of aluminum and magnesium was kept constant as follows: (Al/Mg ratio of 1:3) in HT–glycerol, (Al/Mg ratio of 1:2) in Ti–HT with glycine and glycerol as fuels, (Al/Mg of 1:4) in Zn–HT with glycine and glycerol as fuels.

2.2. Catalyst Activity. Scheme 1 shows the reaction of DMT with EG producing BHET and methanol, and the efficacy of all catalysts is given in Table 2.

2.2.1. Efficacy of Different Catalysts. Zn–HT–glycine, Zn–HT–glycerol, Ti–HT–glycine, Ti–HT–glycerol, and HT–glycerol were used (Figure 2) for the production of
BHET. It was observed that Zn−HT−glycine having mild basicity as well as low acidity in comparison with other studied catalysts showed the best results giving 64.6% conversion of DMT and 96.1% selectivity toward BHET (Table 2).

The results obtained under current investigation are better than those reported in the published literature where the mole ratio of DMT to EG was 1:20.7,8,15 In the current case, it was 1:2 with DMT as the limiting reactant. A blank reaction was conducted without use of any catalyst which showed that the conversion was only 1.7% in 4 h.

For all above catalysts, the conversion and selectivity were confirmed by taking repeated runs to avoid errors and are averaged.

2.3. Effect of Speed of Agitation. Different runs were conducted to study the influence of external mass-transfer resistance on conversion at agitation speed from 800 to 1200 rpm (Figure 3). The conversion increased only marginally with speed and it was practically the same at 1000 and 1200 rpm. Thus, there were no significant effect of mass-transfer resistance on rate of reaction and conversion. A theoretical calculation was also done to find diffusion coefficients, solid–liquid mass-transfer coefficients, and mass-transfer rates in comparison with observed rate of reaction. The rate of mass transfer was very high by an order of magnitude, and hence, there was no mass-transfer resistance. The theoretical background and method of calculation are given elsewhere.32,33 Thus, the subsequent runs were carried out at 1000 rpm.

2.4. Proof of Absence of External Mass-Transfer Resistance. There are different controlling mechanisms as reported in the literature for better understanding of solid–liquid or heterogeneous catalytic reactions. The liquid phase diffusivity of DMT (A) at 180 °C was calculated using Wilke–Chang equation as 1.341 × 10⁻⁵ cm²/s.34 Afterward,
considering the limiting value of Sherwood number (\(Sh_A = k_{SLA} \times d_p/D_{AB}\)) as 2, the mass-transfer coefficient was evaluated as \(3.831 \times 10^{-3} \text{ cm/s}\). The particle surface per unit liquid volume was obtained as

\[
\rho_p = 45.76 \text{ cm}^3/\text{cm}^3
\]

The observed initial rate of reaction for DMT was calculated as \(3.03 \times 10^{-5} \text{ mol cm}^{-3} \text{s}^{-1}\), while the mass-transfer rate for DMT was evaluated as \(6.6 \times 10^{-4} \text{ mol cm}^{-3} \text{s}^{-1}\).

\[As \gg \left[ \frac{1}{r_{\text{obs}} \times k_{\text{SLA}} \times [A_0]} \right] \]

that is, \(3.29 \times 10^4 \gg 1.5 \times 10^3\)

Hence, it proved that there was no external mass-transfer resistance for the reaction. The only resistance could be due to intraparticle diffusion, surface reaction, chemisorption, or desorption. It will be discussed later.

2.5. Effect of Catalyst Loading. The catalyst quantity was varied from 0.05 to 0.15 g/cm³ (Figure 4). The conversion of DMT was found to increase with catalyst loading \(w (g/cm^3)\). A plot was made for initial rate (\(dX/dt\)) versus time which shows that the rate of reaction is directly proportional to the number of available active sites, that is, mass of the catalyst (Figure 5). The Weisz–Prater modulus was also calculated to confirm the absence of intraparticle diffusion limitation and the reaction was kinetically controlled.35

2.6. Proof of Absence of Intraparticle Resistance. Considering 70 \(\mu\)m as the average particle size of the catalyst Zn–HT–glycine, theoretical calculations were performed to calculate the Weisz–Prater criterion (\(C_{np}\)).36 The details of these methods are reported in the literature.37,38 The value of \(C_{np}\) thus obtained is 0.051 which is far less than unity, confirming that the reaction was free from intraparticle diffusion resistance. Thus, the reaction was kinetically controlled which was further confirmed from the evaluation of apparent activation energy as given in Section 2.10.

2.7. Effect of Mole Ratio. The molar concentration of the limiting (DMT) to the excess reactant (EG) was varied from 1:1 to 1:3 at the same catalyst loading per unit volume (Figure 6). The initial rate of reaction increased with concentration.

2.8. Effect of Temperature. Experiments were conducted at different temperatures ranging from 150 to 190 °C (Figure 7). Conversion of DMT increased with temperature. This result indicates that the reaction is controlled by kinetic step only, and mass-transfer and intraparticle diffusion resistances do not play any role during the reaction.

Table 3 gives the comparison of published research on transesterification of DMT with EG for the synthesis of BHET including the current work. Both super base catalysts, viz. Cs₂O/γ-Al₂O₃ and Na₂/NaOH/γ-Al₂O₃ resulted in to 88 and 90% selectivity of BHET, respectively, for 0.25 mol DMT per g of catalyst. However, Zn–HT–glycine in the current work showed 96.1% selectivity toward BHET for 0.072 mol DMT per g of catalyst, which is 3.47 times less. Rest of the catalysts listed in Table 4 are homogeneous in nature. Thus, the current work gives more selectivity toward BHET with the use of cheap heterogeneous base catalyst, Zn–HT–glycine, with excellent selectivity at much lower DMT/EG molar ratio, less DMT/catalyst ratio with reusable catalyst, and in solvent-free condition to make the process green. The volume of reaction mass governs the reaction rate.
2.9. Effect of Reusability of Catalyst. After each experiment, the catalyst was separated by filtration and washed with 50 cm³ methanol to desorb any adsorbed material from the catalyst pores and then dried at 120 °C. Generally, there was a loss of ∼2 to 3% catalyst which was compensated with a fresh catalyst (Figure 8). It was noticed that the catalyst activity and selectivity reduced very marginally on repetitive use of the same catalyst. Further experiments were done where no make up for the loss of catalyst during filtration was done. However, the volume of the reaction mass was reduced to maintain the same catalyst loading in g/cm³ and the same mole of reactants/mass of the catalyst. The experimental results were within ±2% proving that the activity was preserved.

2.10. Reaction Mechanism and Kinetic Model. A kinetic model was developed for the transesterification reaction in the absence of both external mass-transfer and intraparticle diffusion resistances. Out of the many models tried, the following was observed to fit the data reasonably well. In this reaction, chemisorption of A (DMT) and B (EG) takes place on two nearby vacant sites S₁ and S₂, respectively, according to the Langmuir−Hinshelwood−Hougen−Watson (LWHW) mechanism to give E (bis(2-hydroxyethyl terephthalate)) and F (methanol) (Scheme 2).

**Table 3. Comparative Literature of Transesterification of DMT and EG for the Synthesis of BHET with Reference to the Current Work**

| DMT/EG mol ratio | catalyst            | temp (°C) | time (h) | catalyst/reactant ratio | conv. (%) | sel. (%) | refs   |
|------------------|---------------------|-----------|----------|-------------------------|-----------|----------|--------|
| 1:10             | Cs₂O/γ-Al₂O₃ (hetero)| 180       | 2.5      | 0.25 mol DMT/g catalyst  | 100       | 88       | 8      |
| 1:20             | Na/NaOH/γ-Al₂O₃ (hetero) | 180       | 2.5      | 0.25 mol DMT/g catalyst  | 100       | 90       | 8      |
| 2:1              | Mg/Mn/Zn acetate (homo) | 175       | 3        | 2.55 × 10⁴ mol DMT/mol catalyst | 88        | 94       | 15     |
| 2:1              | zinc acetate (homo) | 180       | 3        | 1.83 × 10⁴ mol DMT/mol cat | 20(BHET)  | 15       |
| 2:1              | zinc acetate (homo) | 190       | 4        | 2.5 × 10⁴ mol DMT/mol cat | 76        | 7        |        |
| 1:2              | Zn−HT−glycine (hetero)| 180       | 4        | 0.072 mol DMT/g-cat | 64.1      | 96.1     | current work |

“Selectivity (%) = [moles of desired product/sum of moles of all products] × 100.
In the next step, the surface reaction of complexes takes place giving ES₁ and FS₂ as follows

\[
\text{AS}_1 + \text{BS}_2 \xleftrightarrow{K} \text{ES}_1 + \text{FS}_2
\]  

Finally, desorption of complexes formed ES₁ and FS₂ is represented by following reversible reactions

\[
\text{ES}_1 \xleftrightarrow{1/K_E} \text{E} + \text{S}_1
\]  

\[
\text{FS}_2 \xleftrightarrow{1/K_F} \text{F} + \text{S}_2
\]

It gives regeneration of active sites S₁ and S₂.

If the surface reaction is the rate controlling step, then the rate of reaction of A is given by

\[
-r_A = \frac{-dC_A}{dt} = k_t C_{A_0} C_{B_0} - k_i C_{ES_1} C_{FS_2}
\]  

When the reaction is far away from equilibrium

\[
-r_A = \frac{-dC_A}{dt} = k_r C_{A_0} C_{B_0} = k_r C_{A_1} C_{A_0} C_{S_1} C_{S_2} C_{B_0}
\]

Replacing with total site concentration

\[
C_T = C_{T_1} + C_{T_2}
\]

\[
C_T = C_{S_1}(1 + K_A C_A + K_E C_E) + C_{S_2}(1 + K_B C_B + K_F C_F)
\]

\[
-r_A = \frac{-dC_A}{dt} = \frac{k_r C_{A_0} K_A C_B C_A C_B C_F}{(1 + K_A C_A + K_E C_E)(1 + K_B C_B + K_F C_F)}
\]  

If w is the catalyst loading, then

\[
-r_A = \frac{-dC_A}{dt} = \frac{k_r K_A K_B C_A C_B w}{(1 + K_A C_A + K_E C_E)(1 + K_B C_B + K_F C_F)}
\]  

The adsorption constants \( K_A, K_B, K_B, K_E, \) and \( K_F \) were calculated using Polymath 6 and eq 12 (Table 4). Initial concentration of DMT (\( C_{A_0} \)) and EG (\( C_{B_0} \)) were taken as 3.63 and 7.27 mol L\(^{-1}\), respectively.

The values of adsorption constants were observed to be very small and hence, eq 11 leads to

\[
-r_A = \frac{-dC_A}{dt} = k_2 K_A K_B C_A C_B w
\]  

or

\[
-r_A = \frac{-dC_A}{dt} = k_2 C_A C_B w
\]  

where

\[
k_2 = k_r K_A K_B
\]

Table 4 shows that the adsorption equilibrium constants are negligible, leading to a power law model.

If the initial molar ratio of EG and DMT is \( M = \frac{C_{B_0}}{C_{A_0}} \) at time \( t = 0 \), then eq 14 reduces to a typical second-order equation which can be integrated in terms of fractional conversion \( X_A \) of A as follows

\[
\ln \left( \frac{M - X_A}{M(1 - X_A)} \right) = k_2 w C_{A_0} t = k_2 t
\]

For a fixed catalyst loading \( w \) and initial concentration of A, the pseudo-constant can be written as

\[
k_2 w C_{A_0} = k_p
\]
Thus, plots of \(\ln\left(\frac{M - X_f}{M(1 - X_f)}\right)\) versus \(t\) were made at different temperatures at fixed \(w\) and \(C_{A0}\) (Figure 9) which are straight lines passing through origin. It confirms that reaction is second order and validates the mathematical model. The slopes of these lines at various temperatures were used to make the Arrhenius plot (Figure 10). The apparent activation energy was obtained to be 9.64 kcal/mol which established that the reaction rate was controlled by intrinsic kinetics.

Figure 9. Kinetic plot for typical second-order reaction at different temperatures using Zn–HT–glycine. Reaction conditions: DMT 0.12 mol, EG 0.24 mol, total volume 38.2 cm\(^3\), agitation speed 1000 rpm, catalyst 0.05 g/cm\(^3\) reaction mixture.

3. CONCLUSIONS

Different basic zinc- and titanium-loaded HT catalysts were prepared by using the combustion synthesis method with glycerol and glycine as fuels. The effect of combustion fuel was noticed in the activity of the catalysts which were fully characterized and used in transesterification reaction of DMT with EG to synthesize bis(2-hydroxyethyl)terephthalate. Zn–HT–glycine was observed to be the best catalyst which showed better stability, activity, and selectivity. A mechanism was proposed and kinetics were thoroughly deduced using LHHW model. It was observed that all species are weakly adsorbed leading to the second-order rate equation having activation energy 9.64 kcal/mol. The current reaction was carried out with a novel cheaper zinc-modified HT as the catalyst for the first time to give good selectivity without any use of solvent to make the process green and sustainable. Comparison with the earlier literature shows that the catalyst and process conditions are superior to the previously reported research.

4. MATERIALS AND METHODS

4.1. Chemicals. Aluminum nitrate nonahydrate \((\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O})\), magnesium nitrate hexahydrate \((\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O})\), glycerol, zinc nitrate, glycine, titanium tetraisoproxide, nitric acid (70%), DMT, and EG were purchased from S.D. Fine Chemicals, Mumbai, India. A.R. grade chemicals were employed without any further purification for the synthesis of catalysts and its application.

4.2. Synthesis of Catalysts. 4.2.1. Hydrotalcite. The Mg–Al–O mixed oxide catalyst was made by dissolving \((\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O})\) 0.016 mol and \((\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O})\) 0.048 mol in glycerol (0.051 mol) which was used as fuel in the least amount of water. The Al and Mg nitrate ratio was kept at 1:3. Surplus water was removed by heating the mixture at 80 °C in a crucible. It resulted in to a thick paste which was then placed into a preheated muffle furnace at 500 °C, leading to spontaneous combustion. The solid fluffy material after spontaneous combustion was calcined at 650 °C for 3 h.

Table 5 gives the preparation of Zn- and Ti-loaded catalysts vis-à-vis HT.

4.3. Reaction Setup and Procedure. The transesterification reaction was conducted in a standard cylindrical glass reactor of 100 mL volume with four baffles, overhead stirrer, and reflux condenser. The stirrer was a 45° pitched blade turbine impeller connected to a speed regulator. The reactor was kept in a thermostatic oil bath to maintain the desired temperature. In a typical run, 0.12 mol DMT and 0.24 mol EG were introduced in the reactor. The total volume was 38.2 cm\(^3\), No solvent was used. The reaction mixture was heated to 180 °C at 1000 rpm. The catalyst loading was 0.05 g/cm\(^3\) of total reaction volume. Sampling was done periodically. At the end,

| no. | catalyst-fuel | catalyst abbreviation | Al(NO\(_3\))\(_3\)·9H\(_2\)O (mol) | Mg(NO\(_3\))\(_2\)·6H\(_2\)O (mol) | titanium isopropoxide (mol) | zinc nitrate (mol) | fuel (mol) |
|-----|--------------|------------------------|-----------------|-----------------|-----------------|-----------------|----------|
| 1   | HT–glycerol  | HT                     | 0.016           | 0.048           | 0.008           | 0.008           | 0.008    |
| 2   | TiMg\(_2\)Al\(_2\)O\(_5\) glycine | Ti–HT–glycine         | 0.016           | 0.032           | 0.008           | 0.008           | 0.042    |
| 3   | ZnMg\(_2\)Al\(_2\)O\(_5\) glycine | Zn–HT–glycine         | 0.016           | 0.032           | 0.008           | 0.008           | 0.004    |
| 4   | TiMg\(_2\)Al\(_2\)O\(_5\) glycerol | Ti–HT–glycerol       | 0.016           | 0.032           | 0.008           | 0.008           | 0.004    |
| 5   | ZnMg\(_2\)Al\(_2\)O\(_5\) glycerol | Zn–HT–glycerol       | 0.016           | 0.032           | 0.008           | 0.008           | 0.004    |

*a Slurry thickening temperature 80 °C, combustion temperature 500 °C, calcination temperature 650 °C.
the catalyst was removed from the reaction mixture by centrifugation. High-performance liquid chromatography (HPLC) (Agilent technologies 1260 infinity) was used with C-18 mid-polar capillary column (0.25 mm ID, 30 m), and the reaction progress was monitored. Acetonitrile was used as a mobile phase at a flow rate of 1.0 mL/min. Gas chromatography–mass spectrometry (GC–MS) (PerkinElmer Clarus 500) with capillary column Elite –1 (30 m, 0.25 mm ID) was used for product confirmation. DMT (limiting reactant) conversion was determined.

4.4. Analytical Method. Sampling was done at periodic intervals by reducing the speed of agitation to zero and allowing the catalyst to settle at the bottom of the reactor. Clear liquid samples were prepared by centrifuging them for 5 min. The sample (20 μL) was diluted in a 10 mL standard volumetric flask using the mobile phase. Analysis of the samples was performed over HPLC (Agilent Technology 1260 infinity; autosampler); Hiplex-H column (300 × 7.7 mm, particle size 8 μm; 55 °C column oven temperature, UV–Vis detector at 210 nm, RID at 55 °C cell temperature). A mobile phase of acetonitrile: water (1:1 v/v with 0.1% orthophosphoric acid) solution was used at a flow rate of 1 cm³/min. Fifteen microliter injector volumes were used in the autosampler. Products were confirmed by using GC–MS. The rates and conversions were based on the disappearance of DMT. The conversion of DMT and selectivity to the main product BHET were calculated by HPLC analysis as follows

\[
\text{Conversion (\%)} = \frac{A_0 - A_i}{A_0} \times 100
\]

where \( A_0 \) and \( A_i \) are the area of DMT at time \( t = 0 \) and \( t = i \), respectively. The selectivity was calculated as

\[
\text{Selectivity (\%)} = \frac{A_\text{BHET}}{A_i} \times 100
\]

where \( A_\text{BHET} \) is the area of the desired BHET product and \( A_i \) is the total area of all the products formed in the reaction.

4.5. Catalyst Characterization. All five catalysts were characterized by EDXs (JOEL JSM 6308LA analytical scanning microscope) using 10 kV voltage at a counting rate 519 cps and energy range of 0–20 keV. SEM images were procured at different amplifications. The textural analysis of catalysts was achieved by nitrogen adsorption using Micromeritics ASAP 2020 instrument. 10% v/v CO₂ in He and 10% v/v NH₃ in He temperature programmed desorption (TPD) (micromeritics Autochem 2290) using TCD detector were used to determine basic and acidic site densities of the catalyst, respectively. A Bruker AXS diffractometer D8 advance Cu Kα radiation (\( \lambda = 1.540562 \)) was used to obtain the powder X-ray diffraction (XRD) pattern of catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02230.

Surface area measurement by \( N_2 \) adsorption and pore size analysis and TPD and XRD of Zn–HT–glycine (PDF)

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 NOMENCLATURE

- \( A \), reactant species A, dimethyl terephthalate
- \( B \), reactant species B, ethylene glycol
- \( C_A \), concentration of A, dimethyl terephthalate (mol/L)
- \( C_A^0 \), initial concentration of A in bulk liquid phase (mol/L)
- \( C_{FS2} \), adsorption concentration of A on active site \( S_2 \) (mol/g-cat)
- \( C_B \), concentration of B ethylene glycol (mol/L)
- \( C_B^0 \), initial concentration of B in bulk liquid phase (mol/L)
- \( C_{ES1} \), concentration of E on active site \( S_1 \) (mol/g-cat)
- \( C_E \), concentration of E, product species (mol/L)
- \( C_{E_S2} \), concentration of E on active site of type \( S_2 \) (mol/g-cat)
- \( C_{E_S1} \), concentration of F on active sites of type \( S_1 \) (mol/g-cat)
- \( E \), product species E
- BHET, bis(2-hydroxyethyl)terephthalate
- \( F \), Product species F, methanol
- \( K_A \), adsorption equilibrium constant for A (g-cat/mol)
- \( K_B \), adsorption equilibrium constant for B (g-cat/mol)
- \( K_E \), adsorption equilibrium constant for E (g-cat/mol)
- \( M \), molar ratio of \( C_K/C_A \)
- \( r_A \), rate of reaction (mol L⁻¹ s⁻¹)
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