Volume 24
Number 10
21 May 2022
Pages 3853-4188

Green Chemistry

Cutting-edge research for a greener sustainable future

rsc.li/greenchem

ISSN 1463-9262

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION
Regina Palkovits *et al.*
Chemical recycling of polyhydroxybutyrate and polylactic acid over supported Ru catalysts

Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Chemical recycling of polyhydroxybutyrate and polylactic acid over supported Ru catalysts†

Marcus S. Lehnertz, Joel B. Mensah and Regina Palkovits *

Check for updates

Cite this: *Green Chem.*, 2022, **24**, 3957

Received 17th January 2022,
Accepted 31st March 2022

DOI: 10.1039/d2gc00216g

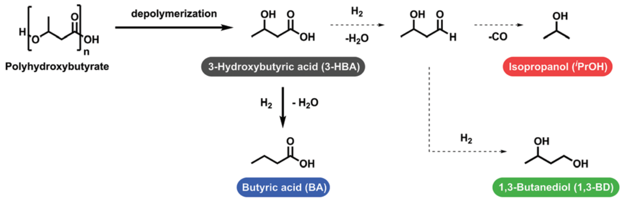
rsc.li/greenchem

Herein, we present a novel protocol for the catalytic depolymerisation of bio-based polyhydroxybutyrate and polylactic acid over Ru/CeO_2. The corresponding monomers of 3-hydroxybutyric acid and lactic acid were afforded with yields of 79 and 94%, respectively. Moreover, the transformation of a mixture of both biopolyesters was possible with a comparable outcome.

Due to the absence of comprehensive circularity in many plastic markets, the majority of today's plastics are still incinerated or landfilled, leading to increasing CO_2 emissions and pollution.[1–5] The contamination leads to serious hazards due to the long degradation periods.[6] For one, microplastics can be harmful to animals and can even enter the human food chain, damaging internal organs. Moreover, the toxicity of respective degradation products and additives as well as the ability of plastic particles to act as pathogen carriers pose further health threats.[7]

Thus, the ongoing shift to renewable feedstocks in the chemical industry for the production of bioplastics should be accompanied by the development of efficient technologies for the chemical recycling and upcycling of these new materials.[8] Two bioplastics already attracting increasing attention are polyhydroxybutyrate (PHB) and polylactic acid (PLA).[9–11] Both biopolyesters can be made from renewable resources *e.g.*, corn, sugar beet, or agricultural waste like whey and are able to degrade in the environment within weeks unlike decades, as for many current industrial polyesters *e.g.*, polyethylene terephthalate (PET) or polycarbonate (PC).[6,12–14] However, here biodegradability should not be seen as a novel robust recycling method but rather as an end-of-life insurance against mismanaged waste streams.[15,16] Moreover, biodegradation is not a particularly attractive closed carbon loop as the carbon is mainly converted into diluted CO_2 streams, which present a challenging entry point into novel value chains. A more attractive way of closing the carbon loop is the direct chemical recycling of bioplastics into the starting monomers.[17] Nevertheless, to this day, mechanical recycling, *i.e.*, melting and re-extrusion of discarded plastics, remains the most prominent strategy. However, this method is sensitive to the heterogeneity of current plastic waste, as it requires rather pure streams. Moreover, this procedure cannot be applied infinitely as the mechanical properties of the downcycled material deteriorate over time.[18,19] More robust processes like pyrolysis allow the processing of less pure feeds but often lead to a rather broad mixture of products.[20] Thus, a chemical recycling into the respective monomers for repolymerisation or subsequent conversion into other chemical building blocks represents a more promising route for closed material cycles (Scheme 1).

Until now, most studies in this field have relied on homogeneous catalytic systems.[21] While this presents a viable entry point for mechanistic insights and offers the advantage of catalysts with high activity and selectivity, one downside of these approaches relates to more elaborate separation steps for catalyst and product recovery. Here, heterogeneous catalysis could complement polymer recycling with molecular systems by offering easy catalyst separation, superior thermal stability, and economic regeneration strategies. Recent studies showcase the general feasibility of depolymerisation using heterogeneous catalysis.[8,22,23] The group of Sun reported the application of Pd/C and Cu/Zn/Al catalysts for PHB depolymerisation under a H_2 atmosphere. A Pd-based catalyst led to the for-



Scheme 1 Proposed reaction network for PHB depolymerisation.

Chair of Heterogeneous Catalysis and Technical Chemistry, Institute for Technical and Macromolecular Chemistry, Worringerweg 2, 52074 Aachen, Germany. E-mail: Palkovits@rwth-aachen.de

† Electronic supplementary information (ESI) available. See DOI: **https://doi.org/10.1039/d2gc00216g**

mation of butyric acid, butanol, butyrates, and gaseous products, whereas a Cu/Zn/Al catalyst was more selective to BA (70% yield).[22]

Reductive PLA depolymerisation using Ru-MACHO-BH, a homogeneous Ru(II) catalyst, was studied by the group of Enthaler, providing 1,2-propanediol yields of up to 99%.[24] Moreover, the uncatalysed thermal depolymerisation of PLA is well-known in the literature. PLA can be recycled to lactic acid (LA) within 30 min, although at the expense of an increased energy demand.[25–27] To the best of our knowledge, no work using a solid supported catalyst has been described for PLA depolymerisation so far. Herein, we report efficient protocols for the chemical recycling of PHB and PLA. For this purpose, we have performed a study of different supported Ru catalysts besides a screening of several reaction conditions to facilitate high monomer yields for repolymerisation and improved circular value-chains.

Supported Ru catalysts are already successfully applied in the depolymerisation of bio-based polymers such as cellulose[28] and formed the basis of this study. The results presented in Table 1 underline the necessity of suitable catalyst selection to obtain the desired C_4-monomers as no yield is observed without a catalyst. It is noteworthy that the total yield does not equal the conversion since gaseous products or higher oligomers were not detectable *via* HPLC analysis.

The screening of the support materials reveals the crucial influence of the catalyst composition with alumina, silica, and zirconia only leading to low total yields of up to 9% (Fig. S1†). Moreover, these catalysts possess a low selectivity towards C_4-products mainly leading to a herein undesired isopropanol (*i*PrOH) formation. Ru dispersed on mixed metal oxides provides higher yet still rather low total yields in the range of 14–16%, except for $MgAl_2O_4$, revealing a total yield of 36% (Table 1). The use of a commercial Ru/C catalyst was also part of the investigations, which led to a total yield of 41%, but only a low 3-hydroxybutyric acid (3-HBA) yield of 6%. A considerably higher catalytic activity was found over CeO_2 and hydrotalcite as support materials. Indeed, the latter reaches a high butyric acid (BA) selectivity of 67% and a significantly higher total yield of 79%. The most promising catalyst of the presented screening is Ru/CeO_2, enabling a total yield of 100% (which corresponds to a yield of 69% for 3-HBA and 31% for BA). It is noteworthy that the ceria support itself exhibits catalytic activity, leading to a total yield of 13%, with a selectivity of 92% towards the 3-HBA monomer. Moreover, Re/CeO_2 is a further promising system, with a high 3-HBA yield of 79% and a 3-HBA selectivity of over 84%. However, the combination of Ru and Re supported on ceria, both with 2.5 wt%, does not lead to improved performance compared to the monometallic materials.

Table 1 Catalyst screening. Conditions: 50 mg of catalyst with a 5 wt% metal loading (~1.5 mol% Ru, ~0.8 mol% Re, or 0.8 mol% Ru and ~0.4 mol% Re for the bimetallic system), 138 mg of PHB, 200 °C, 100 bar H_2, 40 min, 5 ml of H_2O, and 500 rpm

Metal	Support	Y_{Total} [%]	$Y_{\text{3-HBA}}$ [%]	Y_{BA} [%]	$Y_{\text{1,3-BD}}$ [%]	Y_{iPrOH} [%]
—	—	0	0	0	0	0
—	CeO_2	13	12	1	0	0
Ru	$CaZrO_3$	14	7	5	1	1
Ru	$CaTiO_3$	16	5	5	2	4
Ru	$MgAl_2O_4$	36	2	19	2	13
Ru	Carbon	41	6	3	5	27
Ru	Hydrotalcite	79	14	53	2	10
Re	CeO_2	79	67	11	1	0
Ru, Re	CeO_2	90	40	37	4	9
Ru	CeO_2	100	69	31	0	0

To gain further insights into the underlying phenomena governing different catalytic performances, the materials were characterised by temperature programmed reduction (TPR), N_2-physisorption, X-ray diffraction (XRD), and CO-pulse (see Table S1†). The most active material Ru/CeO_2 reveals the lowest main reduction peak temperature of 205 °C in TPR (Fig. S2†). In contrast, the Re-containing catalysts lead to comparable total yields of 79 and 90%, but the reduction temperatures are significantly higher than those for Ru/CeO_2 (324 °C for bimetallic RuRe and 410 °C for monometallic Re). The main reduction peaks for all other catalysts are in the range of 200 to 400 °C. Therefore, no consistent correlation between the reduction temperature and the total yield could be evidenced.

Moreover, further characterisation by N_2-physisorption revealed no relationship between the surface area and the resulting catalytic performance (Table S1†). For instance, Ru/C possesses an almost ten times higher surface area (760 m^2 g^{-1}) compared to Ru/$MgAl_2O_4$ (78 m^2 g^{-1}) yet the total yields are similar (41 *vs.* 36%).

In addition, the metal dispersion was determined by CO-pulse measurements, as it can have a crucial influence on the catalytic activity (Table S1†). Unfortunately, no dispersion values could be derived for Ru/$CaZrO_3$ and Ru/$CaTiO_3$ since only minor amounts of CO were adsorbed. This finding is potentially caused by a too strong metal–support interaction (SMSI-effect) hindering the CO-adsorption.[29–31] The highest metal dispersion with 28% was obtained for the commercial Ru/C catalyst. The relatively high dispersion could be the origin for the high activity in C–C and C–O bond cleavage that this catalyst showed, leading predominantly to *i*PrOH and gaseous products.

In a reference experiment under standard conditions, 10% methane, 7% propane, 1% butane and 8% CO_2 were found by GC-analysis. The distinct activity of Ru/C in decarbonylation as well as further C–C and C–O cleavage has been discussed previously for the hydrogenolysis of biogenic polyols such as sorbitol and xylitol.[32,33] It is noteworthy that the best performing catalyst Ru/CeO_2 possesses one of the lowest dispersions (11%) of all investigated catalysts. In contrast, Re/CeO_2 shows an almost equal 3-HBA yield, despite a significantly higher dispersion of 20%. However, the dispersion is also metal-specific and therefore the comparison of Ru and Re is limited. Overall, the metal dispersion seems to play a subordinate role while the yield and selectivity are mainly influenced by the support composition.

XRD analysis was employed to obtain further insights into the metal particle size. In the case of Ru/CeO_2, additional reflections appear at angles of 25, 31, 34 and 44° (see Fig. S3†). The reflection at 34° can be assigned to the RuO_x species whereas the one at 44° indicates metallic Ru.[34–36] The other catalysts did not reveal these characteristic reflections although an overlapping of reflexes cannot be excluded, especially for $CaTiO_3$ and metallic Ru (see Fig. S4†).

In the following, Ru/CeO_2 was chosen for further optimisation of the reaction, as this catalyst showed the highest activity. For this purpose, a screening of different reaction conditions was executed (Fig. 1) wherein the catalyst amount was decreased to 5 mg of Ru/CeO_2 (0.15 mol% Ru). At this point a reference is made to Fig. S6† where the correlation between the reaction performance and the employed catalyst amounts (1–50 mg) was studied. The data show that the total yield of the observed products (mainly 3-HBA and BA) gradually increases with increasing catalyst amount between 1 and 25 mg Ru/CeO_2. It is noteworthy that for 50 mg the acid yields decrease again at the expense of increased *i*PrOH formation.

The time resolved experiments shown in Fig. 1A revealed that the 3-HBA yield is greatly influenced by the reaction time. First amounts of 3-HBA can be detected after 20 min, increasing further over time to a maximum yield of 79% observed after 110 min, underlining the high activity of the catalyst in the chemical recycling of PHB. Moreover, the importance of a careful choice of the reaction time becomes evident as 3-HBA may be further converted to BA leaving 67% 3-HBA after 240 min. In addition, a decrease of the total yield is visible after 240 min. An analysis of the gaseous phase in a reference experiment conducted for longer reaction times revealed the presence of gaseous products such as methane, propane, and CO_2. These products are believed to be formed through the further degradation of *e.g.* *i*PrOH, BA and crotonic acid (CA). This finding suggests that the formation of gaseous products causes the decrease in the total yield of liquid phase products over time.

Furthermore, the temperature was found to have a crucial influence on the reaction outcome (Fig. 1B). No product formation could be evidenced at 150 °C. The onset of monomer

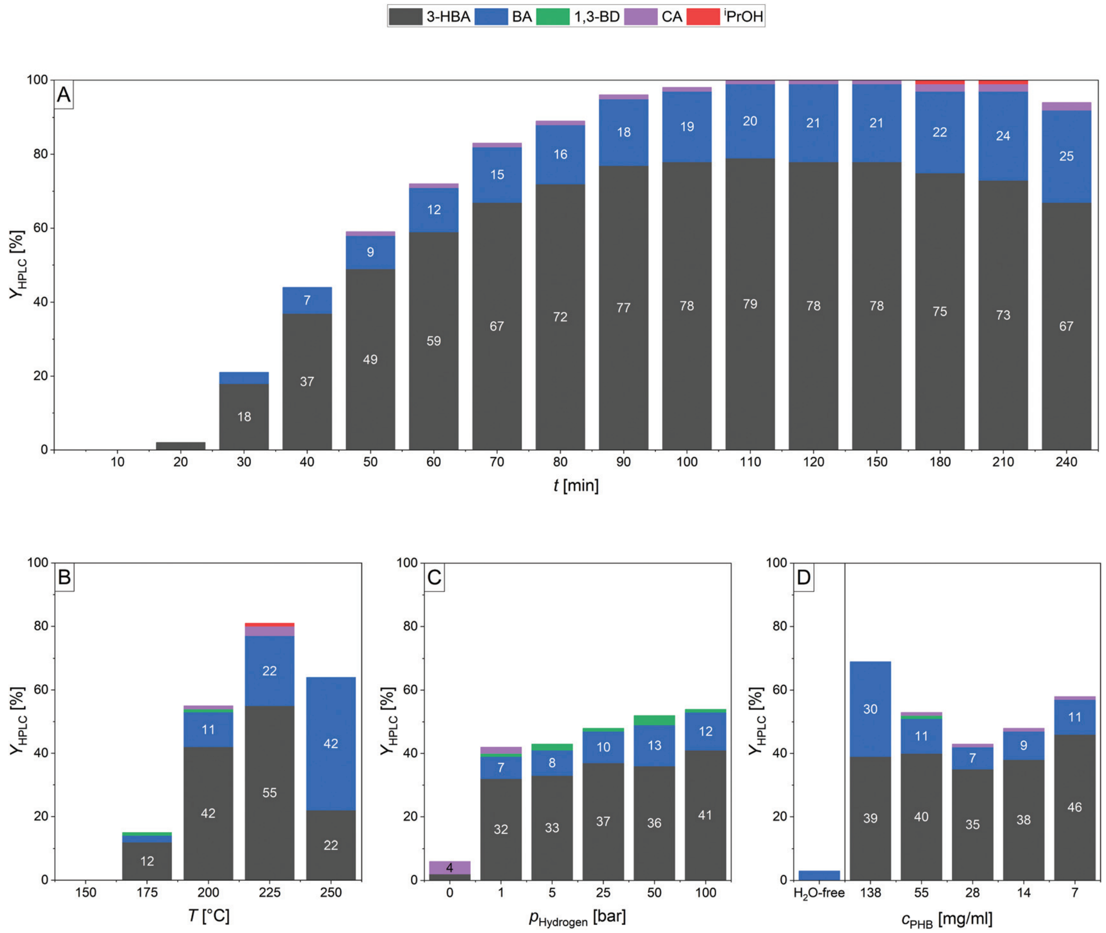


Fig. 1 Investigation of the influence of different reaction parameters; standard conditions for all approaches except as stated otherwise: 138 mg of PHB (1.6 mmol), 5 mg of Ru/CeO_2 (0.0025 mmol Ru), 200 °C, 100 bar H_2, 40 min, 5 ml of H_2O, and 500 rpm. Variations: (A) time: 0–240 min, 414 mg of PHB, 15 mg of Ru/CeO_2, and 15 ml of H_2O; (B) temperature: 150–250 °C; (C) H_2-pressure: 0–100 bar; and (D) polymer concentration by changing the solvent volume: 0–20 ml. Application of HV dried polymer and freshly reduced catalyst in a H_2O-free approach.

production was found to be at around 175 °C, which is also close to the melting point of the polymer.[37] As reported by the group of Sun, a reaction temperature above the melting point seems to be favourable to increase the mass transfer between the solid catalyst and PHB.[22] A further increase of the temperature from 175 to 225 °C leads to improved yields of the C_4-products. At higher temperatures the 3-HBA yield dramatically decreases from 55% at 225 °C to 22% at 250 °C, while the BA yield increases from 22% to 42%. The latter is formed *via* dehydration of 3-HBA to CA[38] and subsequent hydrogenation. A qualitative GC-analysis of the headspace for the reaction at 250 °C detected CO_2 besides methane and propane, indicating a decarboxylation of the acids as previously found for longer reaction times. Hence, conducting the reaction above the polymer melting point at around 180 °C is recommended, facilitating adequate mass transfer between the melted polymer and the solid catalyst. However, the temperature should be kept at approximately 200 °C to avoid the literature-known, herein undesired, dehydration and/or decarboxylation reactions.[38,39]

The crucial role of H_2 in the PHB depolymerisation using Ru/CeO_2 as the catalyst was evidenced by means of a control experiment without H_2 (Fig. 1C). In the absence of H_2, no significant product formation could be detected (2% 3-HBA and 4% CA). In the case of a H_2 atmosphere being applied, the reaction only reveals a low correlation between the pressure and the yields. Comparing 1 and 100 bar, the 3-HBA and BA yields increase from 32 to 41% and from 7 to 12%, respectively. This shows that the increase in pressure is accompanied by an increase in monomer yields, but that even low pressures of only one bar are sufficient to achieve significant conversion towards both 3-HBA and BA. An even higher dependency of the H_2 pressure was revealed for the commercial Ru/C catalyst (Fig. S7†). This different pressure sensitivity indicates that the ceria support ensures a better surface hydrogen availability even at low pressures compared to commercial Ru/C. Thus, higher H_2 pressures can be avoided, enabling a chemical recycling of PHB under milder conditions, which is more attractive for an industrial application reducing investment and operating costs. However, the chemical role of H_2 in the depolymerisation step could not be fully elucidated yet. We propose a hydrogen-assisted formation of protonic acid sites as a potential origin of the enhanced hydrolysis rate in the presence of H_2 and a supported metal catalyst.[40–42]

In the following, the concentration of the polymer starting material was varied (Fig. 1D). This was achieved by using different amounts of an aqueous solvent (0–20 ml). Without water, no significant conversion takes place with only 3% BA being obtained. The highest polymer concentration of 138 mg ml^{-1} leads to the highest total yield of 69% but comes with the drawback of a high BA proportion (30 of 69%). A lower PHB concentration leads to first falling and then rising total yields. However, it should be mentioned that the yield reduction is accompanied by an increase in the selectivity to 3-HBA, it being highest for a concentration of 28 mg ml^{-1}. It can therefore be stated that the concentration of the catalyst and substrate can contribute to the control of the product distribution. The increase in the yields associated with a further decrease in the concentration may be based on an increased polymer dissolution and a higher possibility for the hydrolysis step from PHB to 3-HBA.[43] Moreover, water appears to play an important role in catalyst activity.[44,45] Several studies found that the co-adsorbed water molecules on metallic Ru centers lower the energy barriers facilitating the hydrogenation of the carbonyl groups to the corresponding alcohols.[46–49] Similarly, the depolymerisation of PHB under a H_2-atmosphere could be favored in an aqueous medium due to the dissociation of H_2 on Ru with subsequent spill-over to the support and formation of additional acidic sites.[40–42]

Among the studied catalysts, Ru/CeO_2 shows the best selectivity towards 3-HBA. However, catalyst reusability plays an equally important role besides good catalytic performance. The initially performed recycling runs (Fig. S10†) indicated a gradual deterioration in catalyst performance leading to a decrease in the 3-HBA yield from 75 to 13% after three recycling runs. Hence, strategies to improve catalyst reusability were investigated. For one, the particle size of the ceria support may influence the reusability significantly, as previously demonstrated in stability experiments by the group of Baer.[50] On this account, the effect of bigger support particles was investigated by replacing the CeO_2 support particles of max. 50 nm with those that were max. 5 μm in size. The new Ru/CeO_2 catalyst was then subjected to reusability tests (Fig. S11†). While the increase of the support particles positively impacted catalyst reusability, a less pronounced, yet still apparent deactivation was evident. Moreover, the 3-HBA selectivity significantly decreased after the first reuse. Thus, a re-reduction step after the catalyst recovery was probed as a means to restoring the initial catalytic performance (sixth run). Indeed, this proved to be an effective means of almost fully restoring the initial performance. It is noteworthy that deviations to the first run are found regarding the formation of smaller amounts of CA, indicating a slightly lowered hydrogenation ability. In summary, the use of larger support particles combined with the re-reduction of the catalyst was found as a promising strategy for improved reusability.

Finally, the successful heterogeneously catalysed chemical recycling of PHB into its monomer 3-HBA over Ru/CeO_2 led us to broaden the scope of this method to PLA depolymerisation. PLA is another promising bio-based and bio-degradable material and currently possesses the highest market share for renewably sourced polymers.[9]

As shown in Fig. 2, PLA depolymerisation is also possible in the absence of a catalyst leading to a lactic acid (LA) yield of 98% after 60 min. However, the use of Ru/CeO_2 significantly accelerates this degradation. While the uncatalysed reaction does not show any monomer formation after 10 min, the presence of Ru/CeO_2 leads to a considerable increase in the total yield to 50%, which is dominated by the conversion towards LA (49% yield). With the catalyst, the LA yield increases even further to 94% after only 20 min, whereas only 3% total yield is observed without the catalyst. This highlights the beneficial effect of a catalyst to accelerate the chemical recycling of PLA

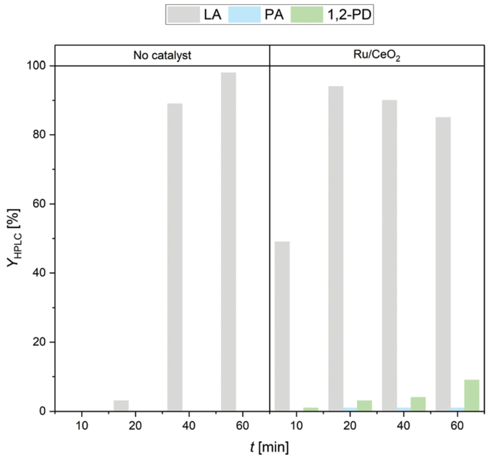


Fig. 2 Catalytic PLA depolymerisation. Conditions: 115 mg of PLA, 25 mg of Ru/CeO_2, 200 °C, 100 bar H_2, 10–60 min, 5 ml of H_2O, and 500 rpm.

into LA. After 40 min a convergence of the yields for the catalysed and uncatalysed reactions was evident. It is noteworthy that in the presence of H_2 some of the produced LA is further converted to 1,2-propanediol (1,2-PD) and propionic acid (PA) over Ru/CeO_2.

Given that robust and economic sorting of plastic waste streams has not been fully developed, the direct application of mixed polyester materials in the catalytic conversion would present a more mature technology with a higher degree of flexibility. In this regard, a combined approach with PHB and PLA was studied in a one-pot reaction. As shown in Fig. 3, the yields for the mixed recycling approach are contrasted with the monomer yields achieved in the corresponding single polymer recycling.

Concerning PHB-derived products, the yields for BA and 3-HBA are reduced from 29 to 24% and from 56 to 46%, respectively. The 1,3-BD yield remains constant at about 2%, while *i*PrOH is only observed in the neat PHB approach with 4% yield. In the case of PLA-based product formation, the observed differences are only minimal. The yields for 1,2-PD and PA vary by only 1%. It is noteworthy that the LA yield even increases from 72 to 77% in the mixed polymer experiment. While the application scope of mixed biopolyesters is accompanied by a slight decrease in the yields of the PHB-derived C_4-products, the data clearly demonstrate the general feasibility of the simultaneous depolymerisation of both polymers over Ru/CeO_2.

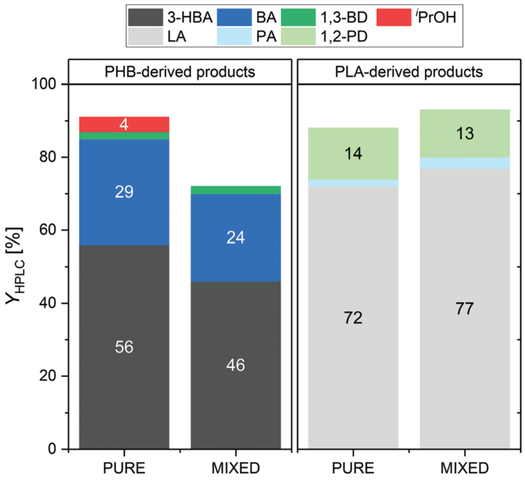


Fig. 3 Mixed polymer approach. Conditions: 73.5 mg of PHB, 57.5 mg of PLA, 25 mg of Ru/CeO_2, 200 °C, 100 bar H_2, 1 h, 5 ml of H_2O, and 500 rpm.

The one-pot catalytic recycling of multiple polyesters was then further extended to PET as a non-bioplastic, which is currently likely to occur in respective waste streams (Fig. S9†). The results reveal that PHB and PLA are converted in a similar manner to the previous mixed recycling approach, whereas PET largely remained intact (96% recovered after filtration, see also Fig. S19†). The low PET conversion is likely related to the significantly higher melting point of PET (*approx.* 250 °C).[51] The results are promising as they indicate the feasibility of the chemical recycling of mixed waste streams comprised of PHB, PLA, and PET. The latter will remain in solid form and could then be easily separated from the reaction solution and depolymerised in a subsequent step tailored to PET, circumventing the need for additional extensive sorting and purification steps prior to the depolymerisation.

In summary, this work reports the catalytic recycling of PHB and PLA into 3-HBA and LA under a H_2 atmosphere in an aqueous phase. With respect to PHB, Ru deposited on ceria exhibited the best performance leading to 3-HBA monomer yields of up to 79% besides 20% BA after 110 min at 200 °C. For longer reaction times or higher reaction temperatures decarboxylation of the monomer acids was observed. The presence of water was found to be crucial as higher amounts of aqueous solvent lead to an increase in 3-HBA selectivity. However, further studies are necessary to elucidate the specific role of potentially more dissolved polymer chains with increased solvent amounts besides the specific interaction of water and Ru/CeO_2 as previously reported in the literature.[46–49]

The substrate scope was also extended to PLA, which led to an accelerated depolymerisation into LA. To the best of our knowledge, this is the first report of the selective PLA depolymerisation into LA over a supported solid catalyst. Our Ru/CeO_2 catalyst gave rise to 94% LA after only 20 min.

Finally, we have demonstrated the direct recycling of a mixed polymer feed comprised of PHB, PLA and PET. Indeed, the described protocol can be used to convert both biopolyesters simultaneously in the presence of large PET amounts, with a similar outcome compared to the respective single polymer approach.

We believe that the herein reported chemical recycling of PHB and PLA proficiently complements conventional mechanical recycling and biodegradation methods to enable full circularity. While mechanical recycling offers finite reprocessing for lower value applications, chemical recycling into the hydroxy acid monomers enables a direct reuse in polymer applications or use as biobased platform chemicals. In this regard, biodegradation (*i.e.*, mainly decomposition of the biopolymers into CO_2 and water) here fulfils the role as a safeguard, in case the polymer material accidentally escapes from the controlled material cycle, rather than serving as primary recycling method.

Nevertheless, future techno-economic and life cycle analyses are required to study and evaluate the overall viability and sustainability metrics of the herein reported methods.

Author contributions

Marcus Lehnertz: conceptualisation, methodology, investigation, validation, visualisation, and writing – original draft. Joel Mensah: conceptualisation, methodology, discussion, writing – review, and suggestions. Regina Palkovits: conceptualisation, methodology, resources, discussion, funding acquisition, writing – review and editing, and supervision.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

We gratefully acknowledge funding by the Exploratory Research Space of RWTH Aachen University (ERS) in the Center for Polymer Recycling (C4PR). This work was performed as part of the Cluster of Excellence Fuel Science Center (EXC 2186, ID: 390919832) funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities. J. B. M. and R. P. thank the European Regional Development Fund (ERDF) and the federal state of North-Rhine Westphalia, Germany for financial support under the operational program 'Regional Competitiveness and Employment' project 'Sustainable Chemical Synthesis'.

The authors thank Christiane Golchert, Adrian Hergesell, Jerome Hommes, Christopher Pütz, Matthias Urban, Jenny Bartzsch, and Frederic Thilmany for contributing to the success of this work through helpful discussions or conducting preliminary experiments as well as the analytical staff members Noah Avraham and Jens Heller for performing HPLC and ICP analyses. We kindly acknowledge ThermoFischer, Paul Mack, and Samir Mammadov for XPS measurements.

Notes and references

1 R. Geyer, J. R. Jambeck and K. L. Law, *Sci. Adv.*, 2017, **3**, e1700782.
2 J. G. J. Olivier and J. A. H. W. Peters, Trends in global CO_2 and total greenhouse gas emissions, *PBL Netherlands Environmental* Assessement Agency, The Hague, 2020.
3 J. R. Jambeck, R. Geyer, C. Wilcox, T. R. Siegler, M. Perryman, A. Andrady, R. Narayan and K. L. Law, *Science*, 2015, **347**, 768–771.
4 M. Bergmann, S. Mützel, S. Primpke, M. B. Tekman, J. Trachsel and G. Gerdts, *Sci. Adv.*, 2019, **5**, eaax1157.
5 N. Ajith, S. Arumugam, S. Parthasarathy, S. Manupoori and S. Janakiraman, *Environ. Sci. Pollut. Res. Int.*, 2020, **27**, 25970–25986.
6 A. Chamas, H. Moon, J. Zheng, Y. Qiu, T. Tabassum, J. H. Jang, M. Abu-Omar, S. L. Scott and S. Suh, *ACS Sustainable Chem. Eng.*, 2020, **8**, 3494–3511.
7 A. D. Vethaak and H. A. Leslie, *Environ. Sci. Technol.*, 2016, **50**, 6825–6826.
8 I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes and B. M. Weckhuysen, *Angew. Chem., Int. Ed.*, 2020, **59**, 15402–15423.
9 H. v. Pogrell, What are bioplastics?, **https://www.european-bioplastics.org/market/**.
10 *PlasticsEurope - Association of Plastic Manufacturers*, Plastics – The facts 2020: An analysis of European plastics production and demand and waste data, Brussels, 2021.
11 The future of plastics (Editorial), *Nat. Commun.*, 2018, **9**, 2157, DOI: **10.1038/s41467-018-04565-2**.
12 A. Getachew and F. Woldesenbet, *BMC Res. Notes*, 2016, **9**, 509.
13 Y. Tokiwa, B. P. Calabia, C. U. Ugwu and S. Aiba, *Int. J. Mol. Sci.*, 2009, **10**, 3722–3742.
14 L. Hou, L. Jia, H. M. Morrison, E. L.-W. Majumder and D. Kumar, *Bioresour. Technol.*, 2021, **342**, 125973.
15 M. F. Cosate de Andrade, P. M. S. Souza, O. Cavalett and A. R. Morales, *J. Polym. Environ.*, 2016, **24**, 372–384.
16 V. Rossi, N. Cleeve-Edwards, L. Lundquist, U. Schenker, C. Dubois, S. Humbert and O. Jolliet, *J. Cleaner Prod.*, 2015, **86**, 132–145.
17 J. Payne, P. McKeown and M. D. Jones, *Polym. Degrad. Stab.*, 2019, **165**, 170–181.
18 M. Frounchi, *Macromol. Symp.*, 1999, **144**, 465–469.
19 H. Jin, J. Gonzalez-Gutierrez, P. Oblak, B. Zupančič and I. Emri, *Polym. Degrad. Stab.*, 2012, **97**, 2262–2272.
20 F. M. Lamberti, L. A. Román-Ramírez and J. Wood, *J. Polym. Environ.*, 2020, **28**, 2551–2571.
21 P. McKeown and M. D. Jones, *Sustainable Chem.*, 2020, **1**, 1–22.
22 H. Zhang, S. Kang, J. Li, Z. Li, J. Chang, Y. Xu, G. Max Lu and C. Sun, *Fuel*, 2021, **286**, 119405.
23 S. Kang, X. Zhang, W. Zhang, W. Li, H. Chen, P. Yang, P. Tang, K. Cheng and Y. Xu, *Energy Fuels*, 2018, **32**, 11639–11644.
24 T. O. Kindler, C. Alberti, E. Fedorenko, N. Santangelo and S. Enthaler, *ChemistryOpen*, 2020, **9**, 401–404.
25 H. Tsuji, H. Daimon and K. Fujie, *Biomacromolecules*, 2003, **4**, 835–840.
26 R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004, **4**, 835–864.
27 R. G. Sinclair, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 1996, **33**, 585–597.

28 R. Palkovits, K. Tajvidi, J. Procelewska, R. Rinaldi and A. Ruppert, *Green Chem.*, 2010, **12**, 972–978.

29 S. Bonanni, K. Aït-Mansour, H. Brune and W. Harbich, *ACS Catal.*, 2011, **1**, 385–389.

30 Z. Wang, J. Lin, R. Wang and K. Wei, *Catal. Commun.*, 2013, **32**, 11–14.

31 S. J. Tauster, S. C. Fung and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170–175.

32 P. J. C. Hausoul, A. K. Beine, L. Neghadar and R. Palkovits, *Catal. Sci. Technol.*, 2017, **7**, 56–63.

33 P. J. Hausoul, L. Negahdar, K. Schute and R. Palkovits, *ChemSusChem*, 2015, **8**, 3323–3330.

34 M. L. Green, M. E. Gross, L. E. Papa, K. J. Schnoes and D. Brasen, *J. Electrochem. Soc.*, 1985, **132**, 2677–2685.

35 A. Salomonsson, R. M. Petoral, K. Uvdal, C. Aulin, P.-O. Käll, L. Ojamäe, M. Strand, M. Sanati and A. L. Spetz, *J. Nanopart. Res.*, 2006, **8**, 899–910.

36 M. C. S. Sierra, J. G. Ruiz, M. G. Proietti and J. Blasco, *J. Mol. Catal. A: Chem.*, 1995, **96**, 65–75.

37 Sigma Aldrich – Merck kGaA, Certificate of analysis – Poly [(R)-3-hydroxybutyric acid], Buchs, 2022.

38 Y. Li and T. J. Strathmann, *Green Chem.*, 2019, **21**, 5586–5597.

39 H. Zhang, S. Kang, J. Li, Z. Li, J. Chang, Y. Xu, G. Max Lu and C. Sun, *Fuel*, 2021, **286**, 119405.

40 H. Hattori and T. Shishido, *Catal. Surv. Jpn.*, 1997, **1**, 205–213.

41 M. García-Melchor and N. López, *J. Phys. Chem. C*, 2014, **118**, 10921–10926.

42 Z. Li, K. Werner, L. Chen, A. Jia, K. Qian, J. Q. Zhong, R. You, L. Wu, L. Zhang, H. Pan, X. P. Wu, X. Q. Gong, S. Shaikhutdinov, W. Huang and H. J. Freund, *Chem. – Eur. J.*, 2021, **27**, 5268–5276.

43 C. Lauzier, J.-F. Revol, E.-M. Debzi and R. H. Marchessault, *Polymer*, 1994, **35**, 4157–4162.

44 Y. Kim, E.-s. Moon, S. Shin and H. Kang, *Angew. Chem.*, 2012, **124**, 12978–12981.

45 J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu and Y. Li, *ChemCatChem*, 2015, **7**, 508–512.

46 B. S. Akpa, C. D'Agostino, L. F. Gladden, K. Hindle, H. Manyar, J. McGregor, R. Li, M. Neurock, N. Sinha, E. H. Stitt, D. Weber, J. A. Zeitler and D. W. Rooney, *J. Catal.*, 2012, **289**, 30–41.

47 H. Wan, A. Vitter, R. V. Chaudhari and B. Subramaniam, *J. Catal.*, 2014, **309**, 174–184.

48 A. Michaelides, A. Alavi and D. A. King, *J. Am. Chem. Soc.*, 2003, **125**, 2746–2755.

49 S. Maier, I. Stass, J. I. Cerda and M. Salmeron, *Phys. Rev. Lett.*, 2014, **112**, 126101.

50 S. Kuchibhatla, A. S. Karakoti, A. E. Vasdekis, C. F. Windisch, Jr., S. Seal, S. Thevuthasan and D. R. Baer, *J. Mater. Res.*, 2019, **34**, 465–473.

51 G. Poulakis and C. D. Papaspyrides, *J. Appl. Polym. Sci.*, 2001, **81**, 91–95.