

Supplementary Information

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

Marcus S. Lehnertz^[a], Joel B. Mensah^[a] and Regina Palkovits^[a]

Experimental

All catalysts were prepared by wet impregnation. If not stated otherwise, the weight percentage of the active component was 5 %. The respective amount of precursor (Ru(III)Cl₃·H₂O and/or NH₄Re(VII)O₄) was dissolved in 20 ml of distilled water. The respective amount of support was then added at once. For instance, in the case of Ru/CeO₂, 266 mg Ru(III)Cl₃·H₂O and 1900 mg of CeO₂ were used. The solution was stirred for 3 h followed by solvent removal under rotary evaporation (60 °C, 30 mbar, 1 h). The dried material was stored under Ar until reduction with molecular H₂. The standard reduction was carried out in a glass tube using an oven (Heraeus instruments, type RO 4/50) at 300 °C for 3 h, with a heating rate of 5 °C·min⁻¹ and a gas flow of 0.1 l·min⁻¹.

The reactions were conducted in 50 ml batch autoclaves equipped with a stirring bar. After the addition of the reaction components, i.e., substrate, catalyst, and solvent the system was flushed three times with H₂ and finally set to the desired H₂ pressure. Afterwards the autoclave was placed in a pre-heated mantle. The reaction time was started once the respective temperature was reached. The reactions were quenched by external cooling with ice water. After a cool-down period of 15 min, the pressure was released. The reaction solution was transferred to a glass vial using a syringe. An additional 1 ml of the respective solvent was used to rinse the autoclave. The as-obtained reaction solution was filtered with PA 45/20 filters (pore size 0.45 µm) to remove the catalyst particles and further product quantification by HPLC was carried out.

To recycle the catalyst, the liquid phase was extracted *via* syringe and filtrated through a polyamide filter delivered by Sartorius with a pore size of 200 nm. The autoclave was rinsed with chloroform to dissolve the remaining PHB. The solution was then also filtrated over the same filter, followed by a washing step with 10 ml acetone to remove the remaining water. Then, the filter cake was washed with a total of 50 ml chloroform and the remaining solid was vacuum dried at 60 °C for 30 min.

The alternative recycling approach for the catalyst was based upon filtration as described previously, but without the acetone and chloroform washing steps. Instead, the remaining catalyst/polymer mixture was transferred into a reduction oven. The temperature was elevated under nitrogen atmosphere to 400 °C with 5 °C·min⁻¹ followed by a re-reduction step under hydrogen for one hour. Afterwards, the catalyst was applied in the next run.

Hot filtration tests broadly followed the usual reaction procedure. However, following the reaction, the solution was filtered with a polyamide filter delivered by Sartorius with a pore size of 200 nm to remove the solid catalyst. The obtained solution was then re-used as reaction solution. In addition, 1.6 mmol fresh polymer was added to the autoclave.

HPLC chromatograms were recorded with a Shimadzu LCMS-2020, equipped with a RI-detector. The flow was set to 2.0 ml·min⁻¹, and the eluent was a mixture of water and TFA with a concentration of 154 µl/l. The organic acid resin column with dimensions of 300 x 8 mm was delivered by CS-chromatography. The oven temperature was set to 40 °C.

¹H-NMR and ¹³C-NMR spectra were recorded at 400 MHz using a Bruker AV400 spectrometer. D₂O and DMSO-d₆ were used as solvent. All measurements were performed at room temperature. The chemical shifts were referenced to the residual solvent signals.

GC-MS measurements have been executed with a ThermoScientific ISQ SingleQuadrupole with 70 eV, an EI, a scan range of 33-500 m/z and a scan time of 0.4 s. The separation of the substrates was performed by a Trance 1310 GC, equipped with a 50 m long Rtx-1-Pona column. The temperature range was 80-250 °C and the heating rate was set to 8 °C·min⁻¹. The eluent flow was set to 1.3 ml·min⁻¹ helium.

Physisorption analysis was carried out using a Quantachrome QuadraSorb and QuadraWin as evaluation software. The specific surface area was calculated using the BET method in the range of $p/p^0 = 0.05-0.4$.

Temperature programmed reduction-profiles (TPR) were recorded with 100 mg of sample and an automated chemisorption analyser called ChemBET Pulsar TPR/TPD, distributed by 3P Instruments. The TCD value was set to 150, the attenuation to 8 and the gas flow, consisting of 10% H₂, was set to 23-24 ml·min⁻¹. The investigated temperature range was 30 to 600 °C.

ICP-MS measurements of the reaction solutions have been performed with an Agilent 8800 ICP-MS/MS Triple Quadrupole. The calibration was executed externally, and the water was acidified to a pH-value of ~ 4 .

Prior to the CO-pulse measurement, the sample with a mass of 100 mg has been reduced at 150 °C using a gas eluent of 5 vol.% H₂/Ar, approx. 25 ml·min⁻¹ for 30 min. The remaining H₂ was removed with a 25 ml·min⁻¹ stream of He at 350°C for 1 h. The CO-adsorption itself took place at room temperature by pulse-like adding CO to the He carrier gas stream (25 ml min⁻¹). Remaining CO was detected *via* a thermal conductivity detector and the uptake of CO was calculated by comparing the theoretical CO-amount without adsorption to the obtained results with the investigated catalyst. Regarding the dispersion calculation, it was assumed that one adsorbed CO-molecule fits one accessible metal atom.

XRD (X-Ray diffraction) patterns have been recorded on a 2nd generation Bruker D2 Phaser using the Cu K- α line as x-ray source.



Figure E1. Left) One of the used 50 ml autoclaves. Right) Experimental approach with 138 mg PHB and 5 mg Ru/CeO₂.

TPR, N₂-Physisorption and CO-Pulse Results

Table S1: Catalyst characterisation *via* TPR, N₂-physisorption and CO-pulse.

Catalyst	$T_{\text{Main reduction peak}}$ [°C]	S_{BET} [m ² g ⁻¹]	Dispersion [%]	Y_{total} [%]
CeO ₂	-	32	-	13
Ru/CaZrO ₃	243	3	n.d.	14
Ru/CaTiO ₃	222	6	n.d.	16
Ru/MgAl ₂ O ₄	293	78	4.8	36
Ru/C	reduced upon delivery	760	27.8	41
Ru/Hydrotalcite	390	30	15.2	79
Re/CeO ₂	410	27	20.4	79
RuRe/CeO ₂	324	25	14.4	90
Ru/CeO ₂	205	22	10.5	100

Experimental results for alumina, silica and zirconia

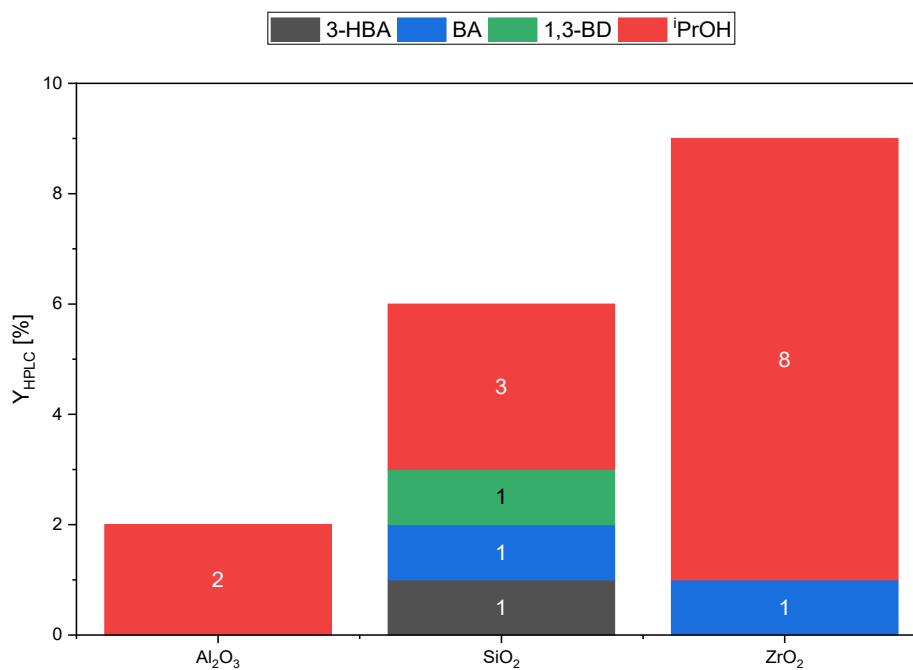


Figure S1. Results for alumina, silica and zirconia supported ruthenium catalysts for the depolymerisation of PHB. Conditions: 50 mg catalyst (~1.6 mol% Ru), 138 mg PHB, 200 °C, 100 bar H₂, 40 min, 5 ml H₂O, 500 rpm.

TPR Spectra for the investigated catalysts

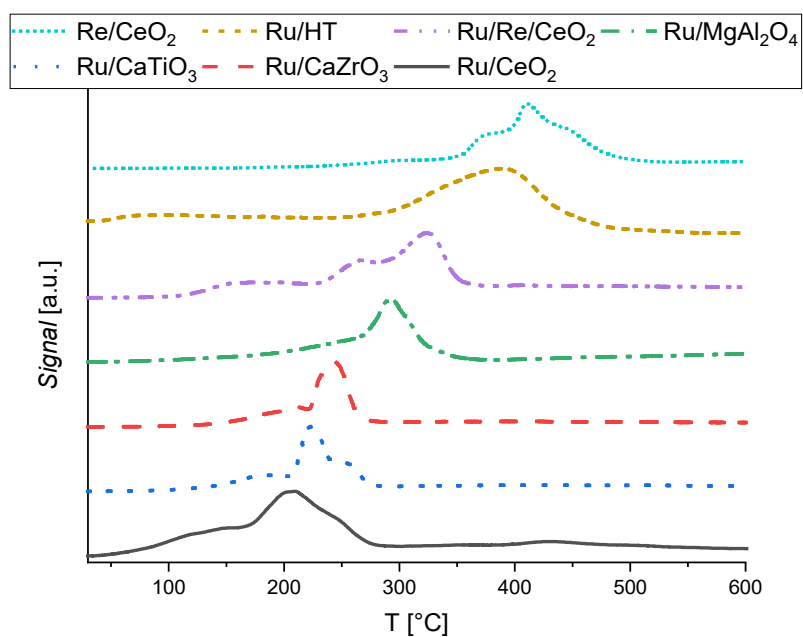


Figure S2. TPR profiles of the applied Ru, Re and Ru/Re catalysts.

XRD Spectra for the investigated supports

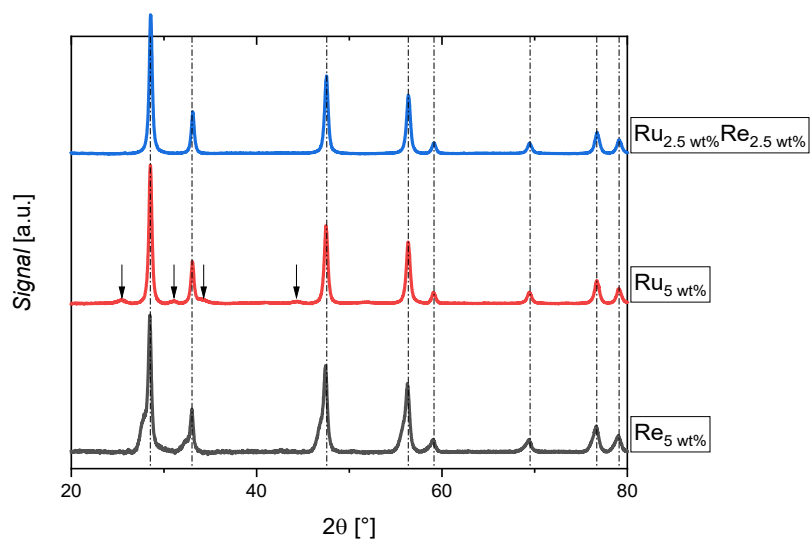


Figure S3. XRD spectra of ceria supported Ru- and Re catalysts. The vertical lines mark the standard reflexes of the ceria support.

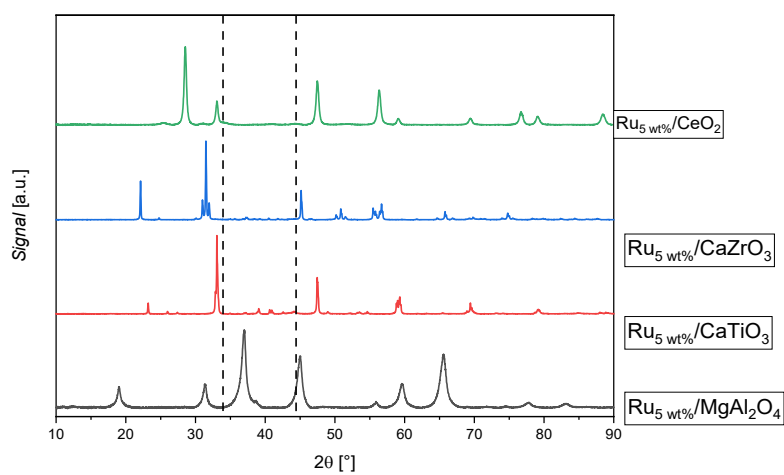


Figure S4. XRD spectra for 5 wt% supported Ru catalysts. The vertical lines mark the reflexes at 34 and 44°.

Further experimental results

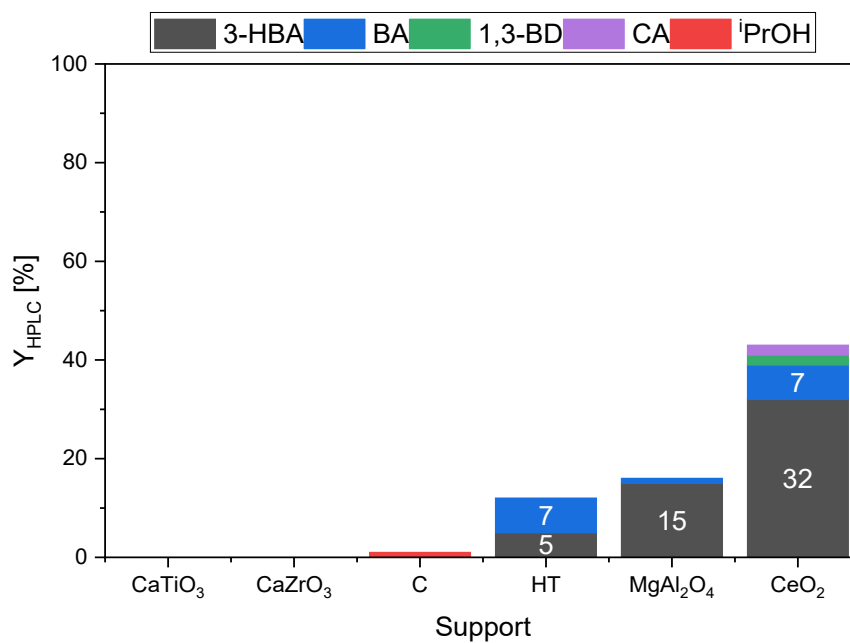


Figure S5. Support screening with 5 mg Ru-catalysts. Conditions: 5 mg Ru/CeO₂, 138 mg PHB, 200 °C, 100 bar H₂, 40 min, 5 ml H₂O, 500 rpm.

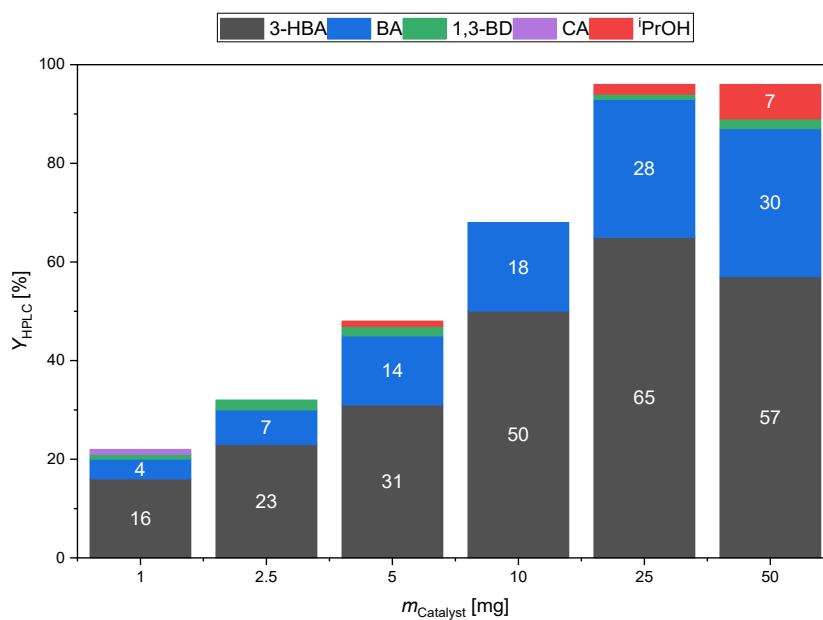


Figure S6. Catalyst amount variation for the best performing Ru/CeO₂ catalyst. Conditions: 1 - 50 mg Ru/CeO₂, 138 mg PHB, 200 °C, 100 bar H₂, 40 min, 5 ml H₂O, 500 rpm.

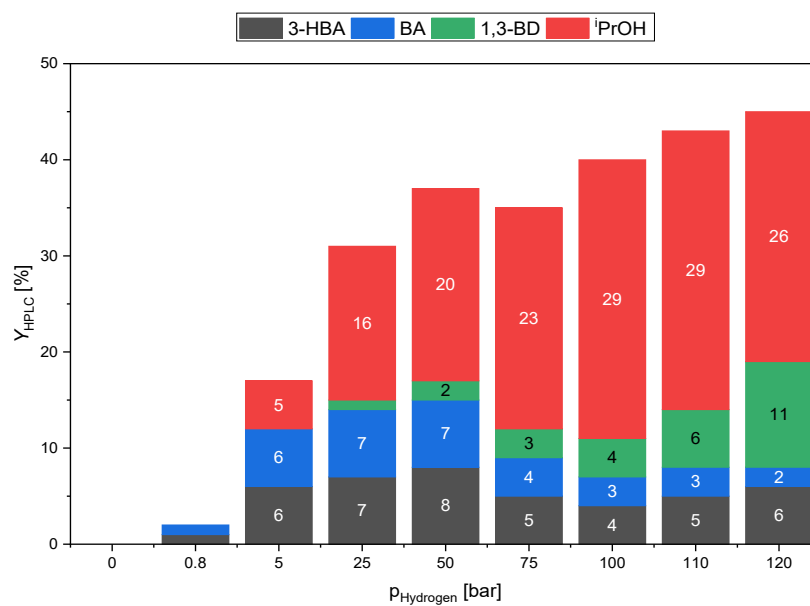


Figure S7. H₂ pressure dependency for the Ru/C Sigma catalyst. Conditions: 50 mg catalyst (~1.6 mol% Ru), 138 mg PHB, 200 °C, 0–120 bar H₂, 40 min, 5 ml H₂O, 500 rpm.

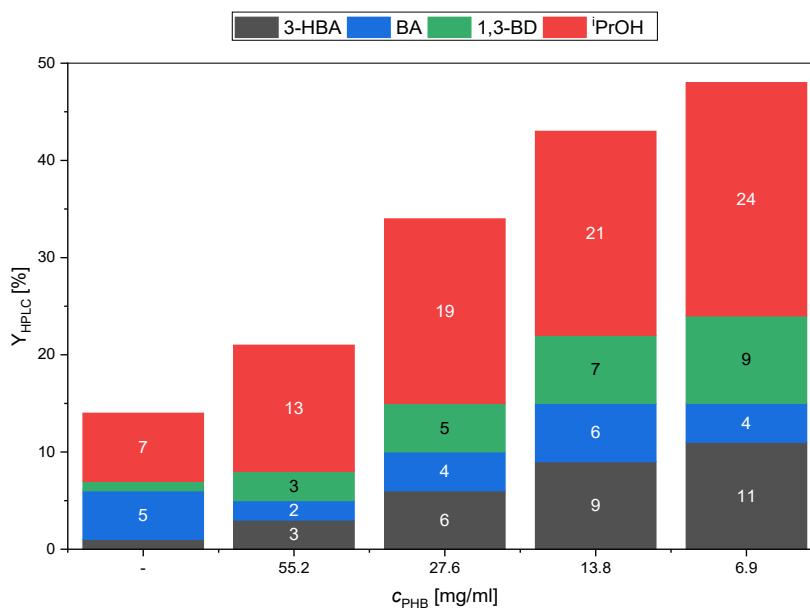


Figure S8. Variation of PHB concentration. Conditions: 50 mg Ru/C (~1.6 mol% Ru), 138 mg PHB, 200 °C, 100 bar H₂, 40 min, 0–20 ml H₂O, 500 rpm.

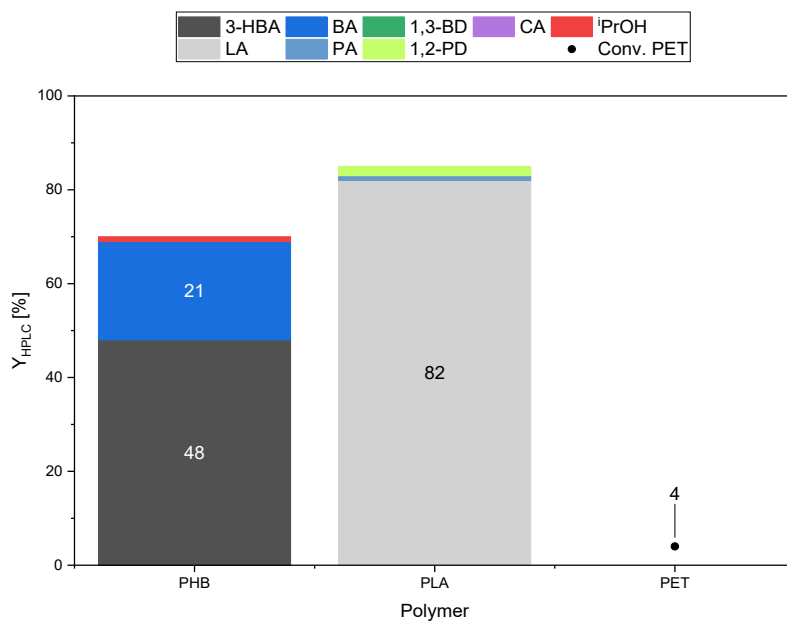


Figure S9. Combined recycling approach with PHB, PLA, and PET. Conditions: 5 mg Ru/CeO₂, 45.7 mg PHB, 38.2 mg PLA, 101.9 mg PET (0.53 mmol each), 200 °C, 100 bar H₂, 5 ml H₂O, 500 rpm.

Catalyst recycling

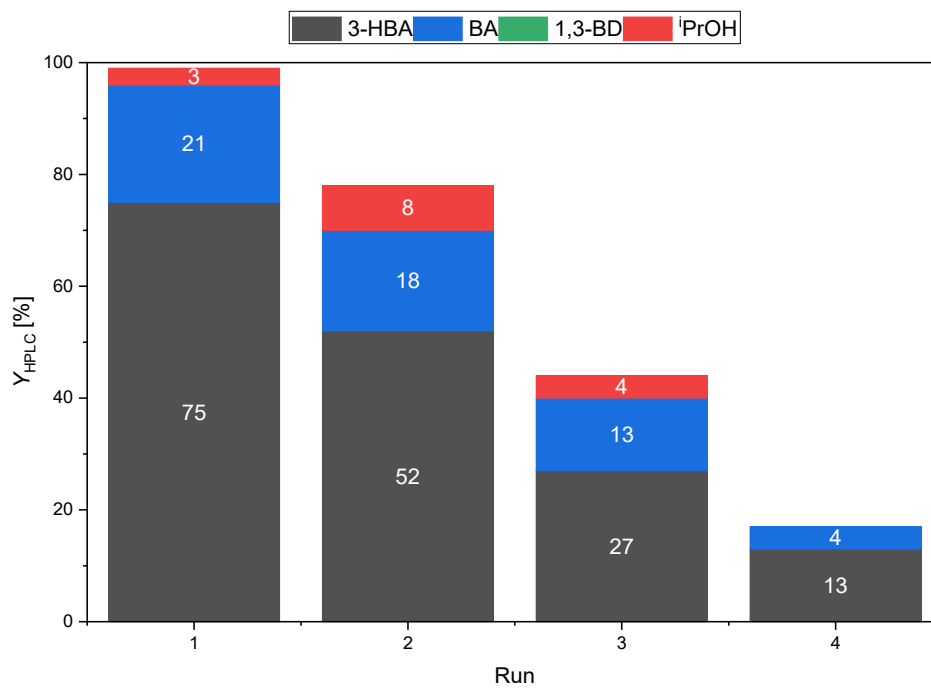


Figure S10. Results after each recycling step of the Ru/CeO₂ catalyst. Conditions: ~1.6 mol% Ru in relation to PHB – kept constant, 200 °C, 100 bar H₂, 25 min, H₂O, 500 rpm.

Besides catalytic properties themselves, the recycling of catalysts gives an insight in their long-time stability and chemical resistance. Therefore, recycling runs were carried out (**Figure S10**). A constant decrease of the total and the respective yields is observed. 75% 3-HBA are obtained after the first run relative to 13% after the fourth run. Leaching was contemplated as possible reason for deactivation. The question remained if this leaching is caused by the reaction conditions itself or by the washing steps (water, acetone and chloroform) during the reusability test.

This issue was assessed through an analysis of the fresh and spent catalyst *via* XPS (see **Figure S12 and S13**). In the case of ceria support (**Figure S12A**), the most significant change is the lower relative intensity of the peaks at 904 and 885 eV, related to Ce(III), indicating the oxidation of the support.^{1,2} The acidic aqueous solvent as well as the presence of hydrogen throughout the reaction should prevent ceria from being oxidized.^{3,4} However, the oxidation of ceria could take place after the reaction by opening the autoclave and thus exposure to an oxidative atmosphere.⁵ Accordingly, oxidation of the catalyst and thereby especially the support may be one reason for reduced activity upon recycling. One approach to solve this issue is the re-reduction of the catalyst after each run (results presented in **Figure S14**). The results remain relatively constant up to the third run, followed by a strong decrease of activity in the fourth. However, the re-reduction and thus regeneration of the catalyst seems to be a possible path, even if it does not address the leaching challenge described in the next paragraph.

The leaching of the catalyst was further investigated with ICP-OES. It was found that ruthenium leached by 0.9% under standard reaction conditions. This low percentual decrease may contribute to the reduced reaction performance over each recycling step but it is unlikely that leaching of the active species is the predominant factor reducing the catalytic performance. Besides leaching or oxidation, residual PHB, which was not removed by the washing step, could lead to an overestimation of the catalyst mass and thus reduce the obtained yields. To investigate this matter, TGA analysis was carried out to estimate the residual PHB amount after the washing step (see **Figure S15**). It was found that the catalyst amount is overestimated by 10 wt% after the fourth run.

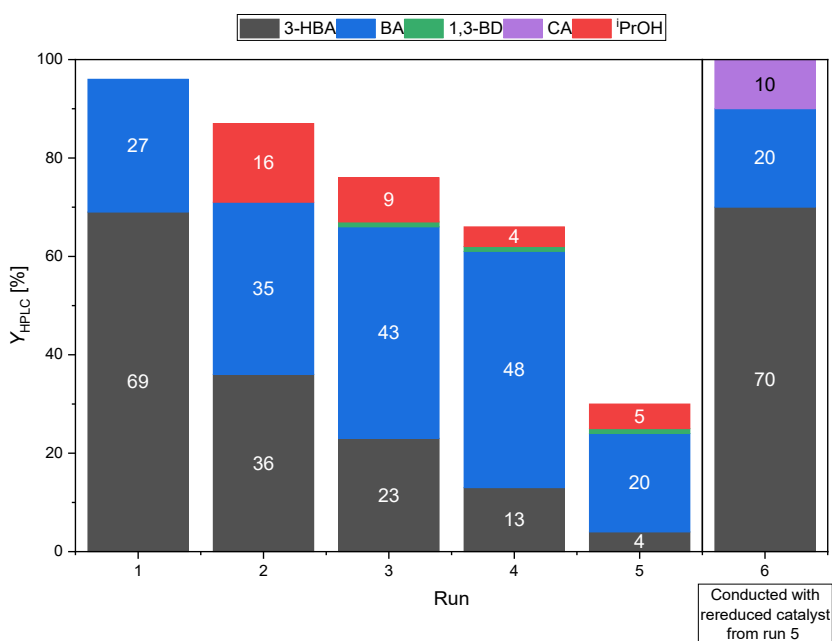


Figure S11. Recycling of Ru/CeO₂ with ceria particles below 5 μm. Runs 1 to 5 without re-reduction. PHB amount adapted to lower catalyst amount after each step. Conditions: ~1.6 mol% Ru in relation to PHB - kept constant, 200 °C, 100 bar H₂, 40 min, 5 ml H₂O, 500 rpm.

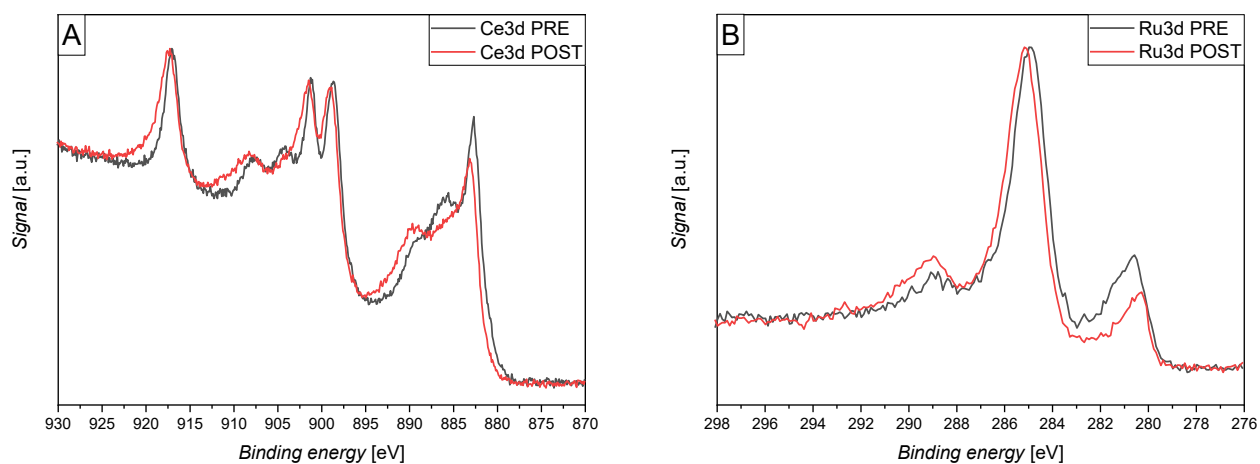


Figure S12. XPS spectra of A) Ce 3d and B) Ru 3d prior and after the reaction. Normalised spectra for direct comparison.

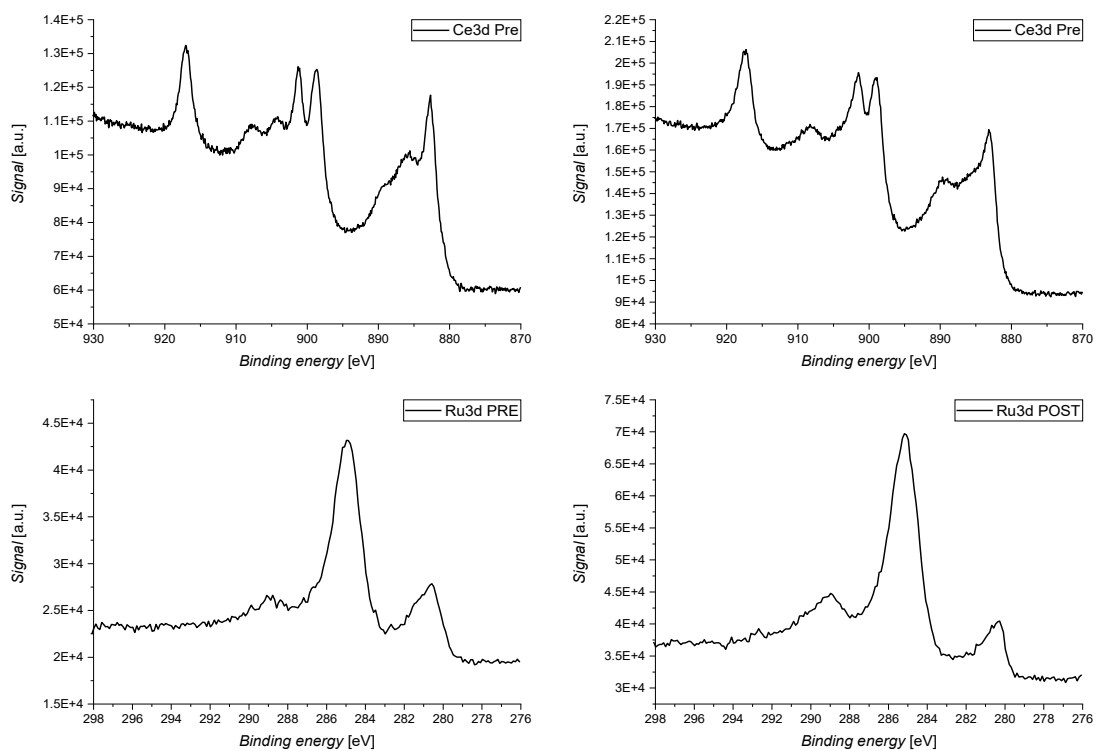


Figure S13. XPS Spectra of fresh and spent Ru/CeO₂ catalyst.

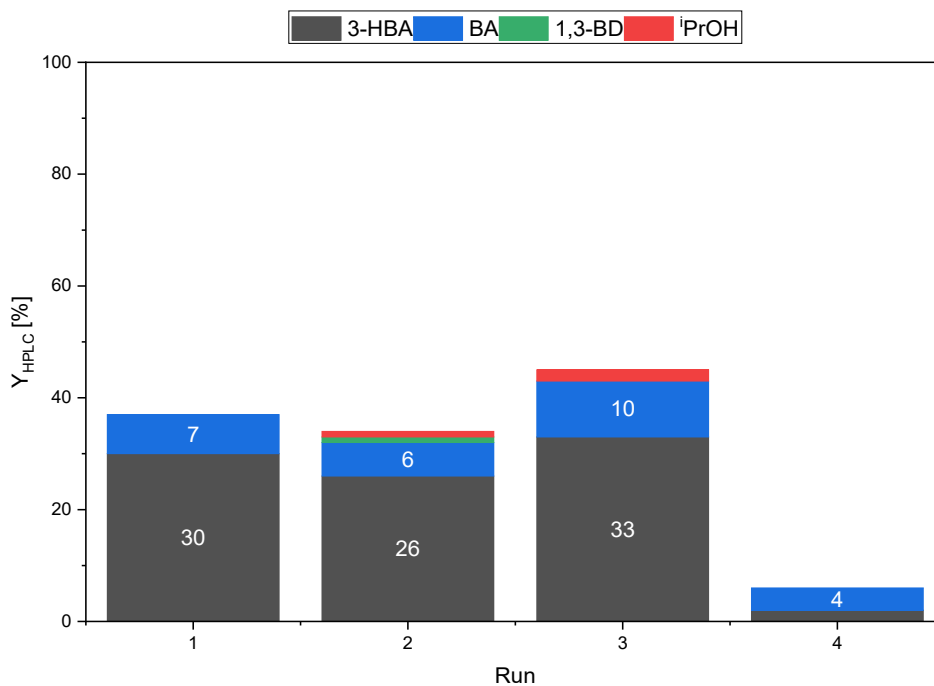


Figure S14. Catalyst recycling runs with regeneration of the Ru/CeO₂ catalyst (<50 nm particle size) in a reduction oven after each step. Conditions: ~1 mol% Ru in relation to PHB – kept constant, 200 °C, 10 bar H₂, 20 min, 20 ml H₂O, 500 rpm.

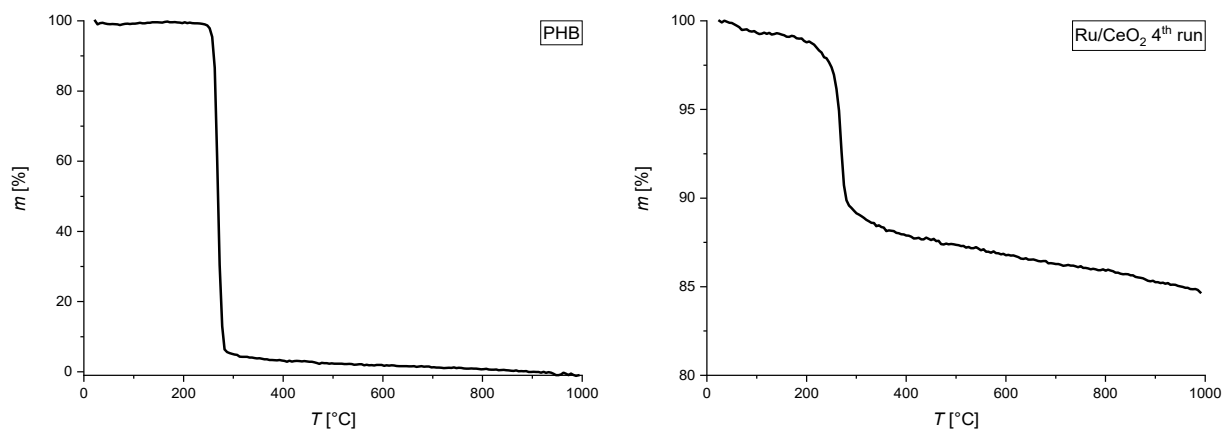


Figure S15. TG-analysis of neat polymer and the Ru/CeO₂ catalyst after four runs.

Active Species

To ensure that the catalytic activity is not based on the formation of a homogeneously active species during the reaction, a hot filtration test has been conducted. The usual procedure of a hot filtration test, i.e. filtering at about 50% conversion and then continuing the reaction, cannot be used here since the polymer is a solid and thus also remains in the filter together with the catalyst. As a limitation, it should be mentioned that PHB is sensitive to acid/base-catalyzed hydrolysis. Therefore, small increases in conversion are to be expected, especially since the pH-value is lowered to 4 by the resulting products of the first reaction, in particular 3-HBA and BA. However, this influence should by far not lead to similarly high conversion as with catalyst since prior experiments to this regard showed only 2% 3-HBA after 1.5 h without catalyst under otherwise identical conditions.

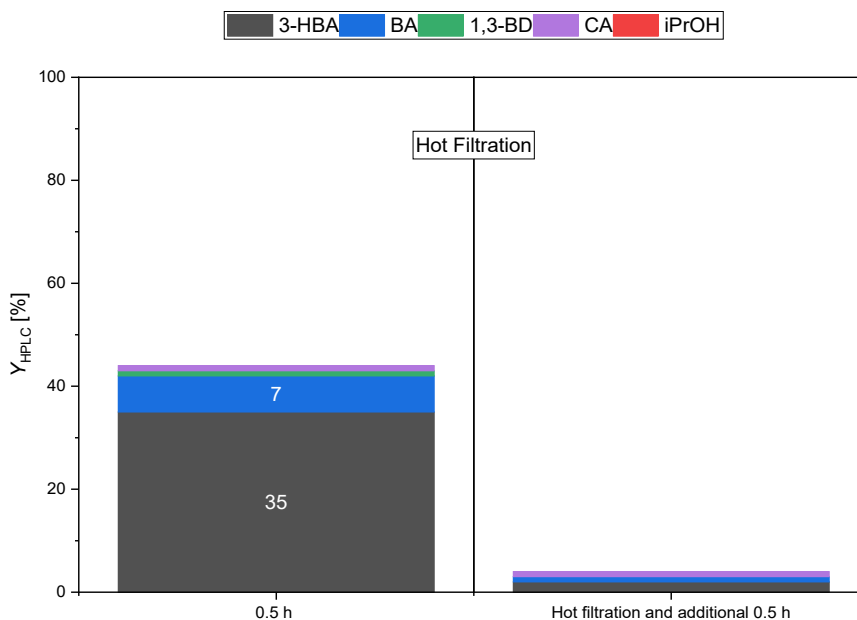


Figure S17. Hot filtration test. Conditions: 5 mg catalyst (~0.16 mol% Ru), 138 mg PHB added initially and again after the hot filtration, 200 °C, 100 bar H₂, 30 min before and after hot filtration, 5 ml H₂O, 500 rpm.

The results presented in **Figure S17** demonstrate that there is no significant increase in the obtained yields after the filtration and the addition of fresh polymer. The addition of fresh polymer is mandatory since the catalyst as well as the polymer were filtered in the hot filtration approach. Unreacted polymer remains solid below the polymers melting point of around 180 °C and thus needs to be re-added to the reaction to enable conversion at all. The yields of 3-HBA and CA increase by 2 and 1%, respectively, whereas the one of BA and 1,3-BD decrease by 1% each. Thus, it can be stated that the observed acceleration of the reaction is indeed based on the solid catalyst.

Moreover, experiments with the possible leaching species Ce(OH)₄ have been conducted up to 4 h (**Figure S18**). A comparison to the results obtained with the Ru_{5 wt%}/CeO₂ catalyst reveals that this ceria species indeed seems to show activity, but far below the solid catalyst since the yields rise after much longer reaction times. Autocatalysis should also be taken into account since the polymer tends to degrade even without additives. Therefore, the combination of all the data conclusively suggests that the acceleration of the reaction is based on the solid catalyst and not on leached species.

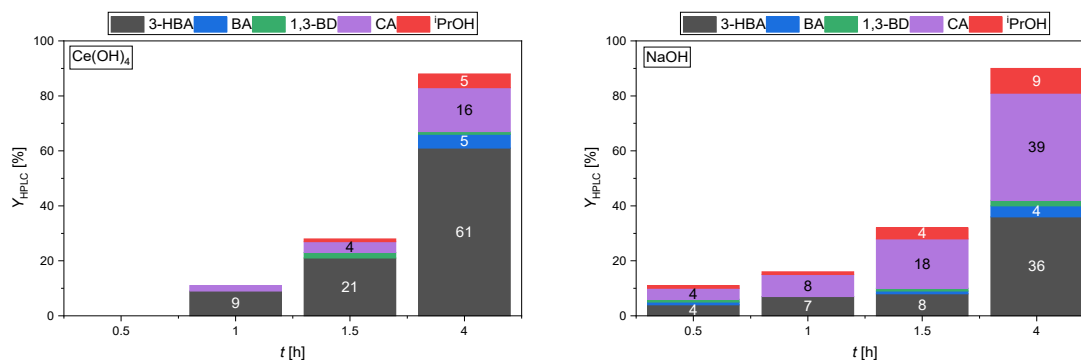


Figure S18. Reaction with the homogeneous species Ce(OH)₄ and NaOH as possible catalyst. Conditions: 5 mg Ce(OH)₄ or NaOH, 138 mg PHB, 200 °C, 100 bar H₂, 0.5 - 4 h, 5 ml H₂O, 500 rpm.



Figure S19. Picture taken after the PHB, PLA and PET recycling approach. Reaction solution has been deducted. The remaining polymer fragments (After reaction 97.6 mg – initially 101.9 mg) are made of PET.

References

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