Supplementary Information (SI) for Green Chemistry.
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Monomer recycling of virgin polycarbonate (PC), end-of-life PC and PC-ABS blends by Ni-catalyzed reductive depolymerization

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1. Materials:

- Ruthenium, 5% on alumina - 5% Ru, dry powder (0.3 wt.% H_2O) – Heraeus
- Palladium, 5% on Alumina - extent of labeling: 5 wt. % loading, powder – Sigma-Aldrich
- Nickel on silica/alumina - extent of labeling: ~65 wt. % loading, powder – Sigma-Aldrich
- PC pellets (3 x 3 x 2 mm) were received from Trinseo (Mw and PDI of 51000 g/mol and 2.2)
- EOL-PC and TV waste (EOL PC-ABS) were collected from the local recycling centers in Belgium

2. Methods:

2.1 Preparation of Ni-supported catalysts:

Wet impregnation was employed for Ni deposition on alumina surface. In short, appropriate amounts of $Ni(NO_3)_2·6.H_2O$ were dissolved in 0.4 ml distilled water. This solution was added dropwise to the corresponding amount of alumina (Aluminum oxide - fused, powder, primarily α-phase, 100-200 mesh – Sigma Aldrich) before drying at 120 ºC overnight. Finally, the samples were calcined in an oven at 450 °C for 4 h to obtain the samples 5, 10, 15 and 20 wt.% NiO/Alumina. In a subsequent step, the samples were reduced under a flow of 100 sccm He + 100 sccm H_2 during following a heating profile of 1 °C/min until 500 or 800 °C, then staying at that temperature for 2 h, before colling down at 5 °C/h. After reduction, the samples 5, 10, 15 and 20 wt.% Ni/Alumina were obtained.

2.2 Reductive depolymerization of polycarbonate (PC):

A 100 ml high-pressure batch reactor (Premex) was used for the reductive depolymerization of polycarbonate. To this end, the reactor was filled with 4.6 g of polymer and 46 g of THF. Then, required amounts of metal-supported catalyst were loaded and the reactor was sealed, pressurized with H_2, heated to the desired temperature and stirred at 750 rpm for a specific time. The upscaled reaction (100 g of plastic) was performed in a Parr 4534 2L Titanium Floor Stand Pressure Reactor coupled with a 4848 Reactor Controller. After completion of the reactions, the reactors were cooled down in a water bath and opened to collect the product mixture, which was filtrated and left to rest overnight. For determination of the PC conversion, 10 ml of the product mixture were added to 50 ml of methanol under vigorous stirring for 30 minutes. The precipitated polymer was recovered by an additional filtration and the conversion was calculated by comparing it to the initial PC mass. The product mixture was analysed by gas chromatography (GC) in a system equipped with a combi-pal series injector, DB5-MS column (60 m x 0.25 mm ID x 0.25 mm), and a flame ionization detector (FID) operating at 310 °C. The Chromeleon software was used for the analysis. An automated injector injected 1 μL of sample with a split ratio 14.3 at a split flow 10. The injection port and initial oven temperatures were 300 °C and 40 °C, respectively. The oven temperature was increased and kept constant for 13 min at 265 °C, for a total run 5 time of 30 min. The specific amounts of each product were determined by a calibration curve.

3. Catalyst characterization:

X-ray diffraction: X-ray diffraction patterns were collected on a Philips/Panalytical X'Pert Pro diffractometer using a Cu-Kα X-ray source (λ = 0.15418 nm).

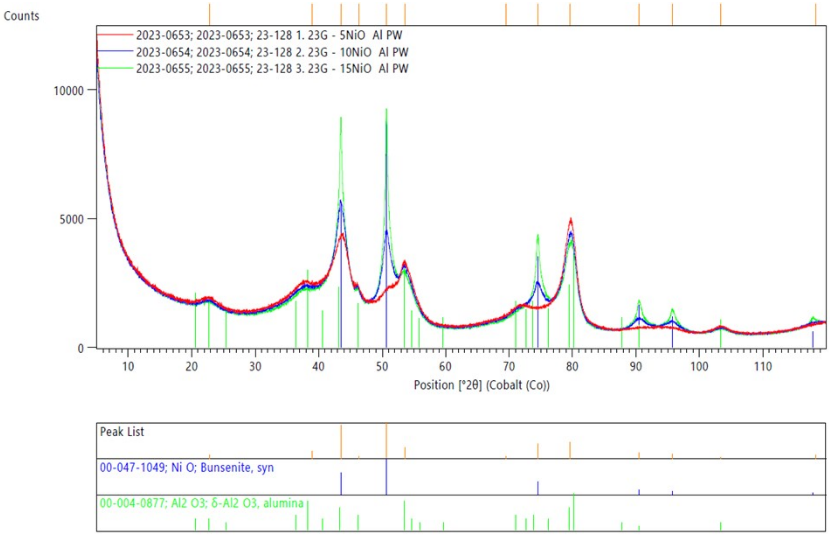

Fig. S1. X-ray diffractogram of samples 5, 10 and 15 wt.% NiO over alumina.

N_2 Physisorption (BET area): N_2 physisorption measurements were carried out at -196 °C using a Micromeritics TriStar II instrument. Prior to measurement, the commercial 66Ni/SiO_2-Al_2O_3 catalyst was degassed at 300 °C for 6 h (ramp rate 10 °C/min) with a SMART Prep 065 under a N_2 atmosphere. The data was analyzed using Microactive software V3.00. The BET (Brunauer-Emmett-Teller) method was used to calculate the surface area and the t plot method was used to determine the external surface area. The Barrett-Joyner-Halenda (BJH) method was used to determine total pore volume (ml/g) and pore diameter (Å).

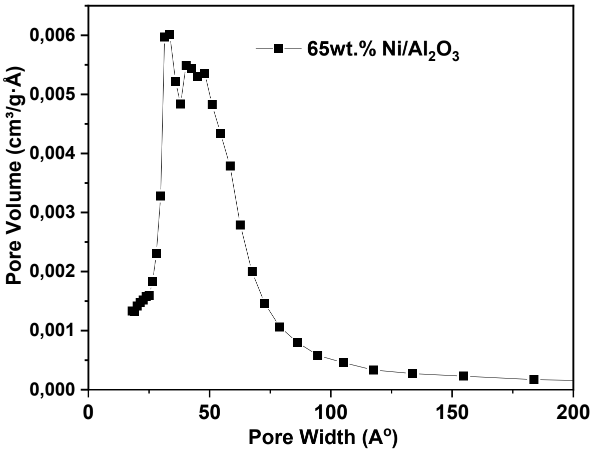

Fig. S2. Pore size distribution of commercial 66Ni/SiO_2-Al_2O_3 catalyst. BET area = 159.5 m^2/g, total pore volume = 0.2628 ml/g and total pore diameter = 53 Å.

Temperature programmed reduction (H_2-TPR): In TPR analysis, the reducibility of the commercial 66Ni/SiO_2-Al_2O_3 catalyst was tested using hydrogen gas (10% H_2 + 90% Ar). In brief, 100 mg of the catalyst were loaded into a U-shaped quartz tube exposed to H_2 gas (60 ml/min) (Autochem 2920, Micromeritics) and heated from room temperature to 900 °C at a rate of 10 °C/min. A thermal conductivity detector was used to measure the outlet gas composition as a function of temperature and time. The TPR profile of the commercial 66Ni/SiO_2-Al_2O_3 catalyst shows two reduction peaks, at 340 and 545 °C. The reduction of NiO weakly interacting with the support is responsible for the peak at 340 °C, while the reduction peak at 545 ºC corresponds to NiO interacting strongly with the support.[1]

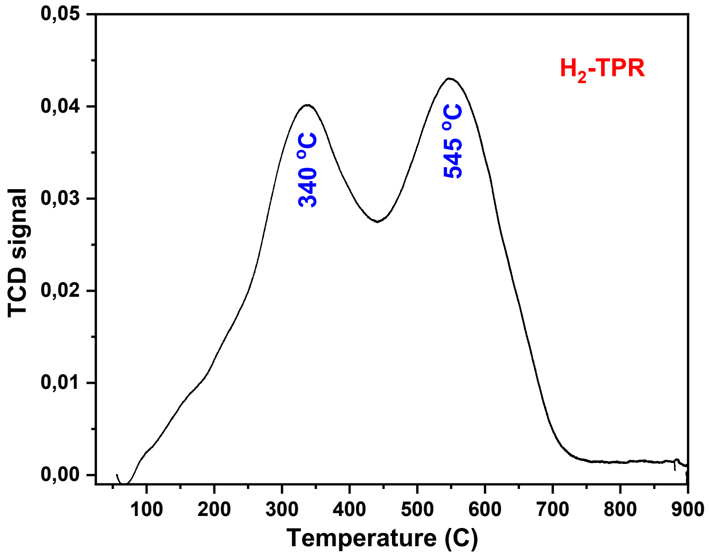

Fig. S3. Temperature programmed reduction profile of the commercial 66Ni/SiO_2-Al_2O_3 catalyst.

Scanning electron microscope - Energy-dispersive X-ray spectroscopy (SEM-EDS):

Scanning Electron microscopy (SEM) images were collected on a FEGFEI Nova NanoSEM 450 at an accelerating voltage of 5 kV. The distribution of the different elements was measured using energy dispersive X-ray (EDX) spectroscopy (QUANTAX 200 EDX, Bruker with an XFlash 5030 SDD detector).

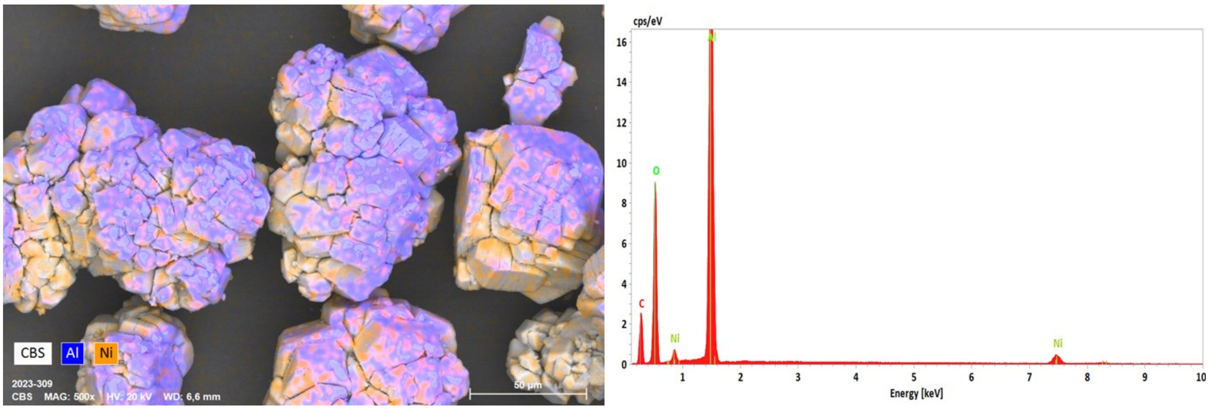

Fig. S4. Scanning electron microscopy (SEM) picture, energy dispersive X-ray spectroscopy (EDS) spectra (right) and elemental mapping of Al and Ni (left) of the sample 5Ni/Al_2O_3. Ni content: 5 wt.%.

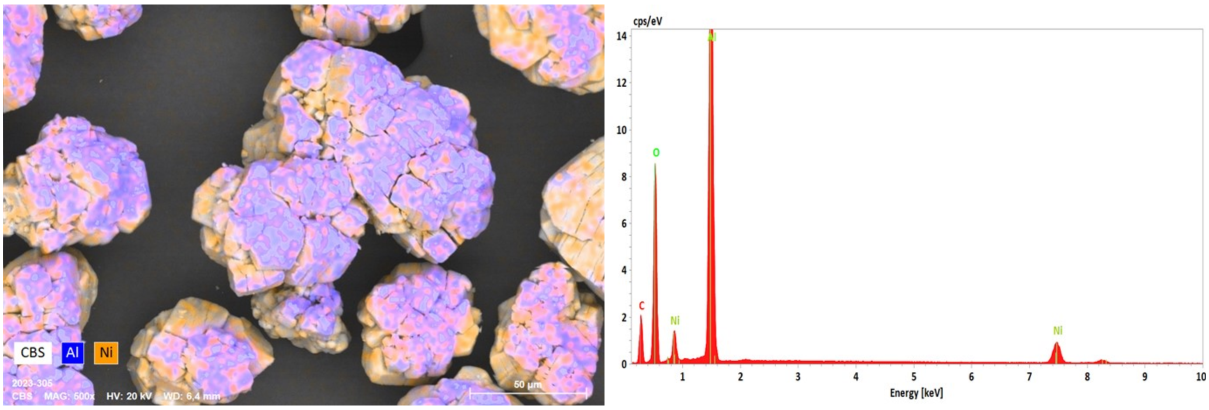

Fig. S5. Scanning electron microscopy (SEM) picture, energy dispersive X-ray spectroscopy (EDS) spectra (right) and elemental mapping of Al and Ni (left) of the sample 10Ni/Al_2O_3. Ni content: 10 wt.%.

Transmission electron microscopy (TEM):

High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) analysis were performed using a JEOL ARM200F probe-corrected microscope, operated at 200 kV and equipped with a cold-field emission gun and the large-angle SDD-EDX detector (Centurio, JEOL), to determine the elemental distribution within the reduced samples. TEM samples were prepared by placing a droplet of the colloidal dispersion of the sample in isopropanol on a holey carbon-coated copper grid. Bright field scanning transmission electron microscopy (STEM), conducted using a JEOL JEM-2200FS, Cs-corrected microscope operated at 200 kV, was used to determine the particle size distribution of reduced samples. For each sample, a Lacey formvar/carbon film supported on a 200 mesh copper grid was immersed in the sample powder. After several minutes of contact time with the powder, the grid was removed and redundant powder was blown off before loading the grid into the microscope specimen holder.

TEM images (Light Mode/Dark Mode), particle size, elemental mapping, and histograms of the prepared 5Ni/Al_2O_3 catalyst are shown in Fig. S6. In TEM images, many darker spots can be observed, identified as Ni particles. Average size of Ni particles was found to be 4.82 nm.

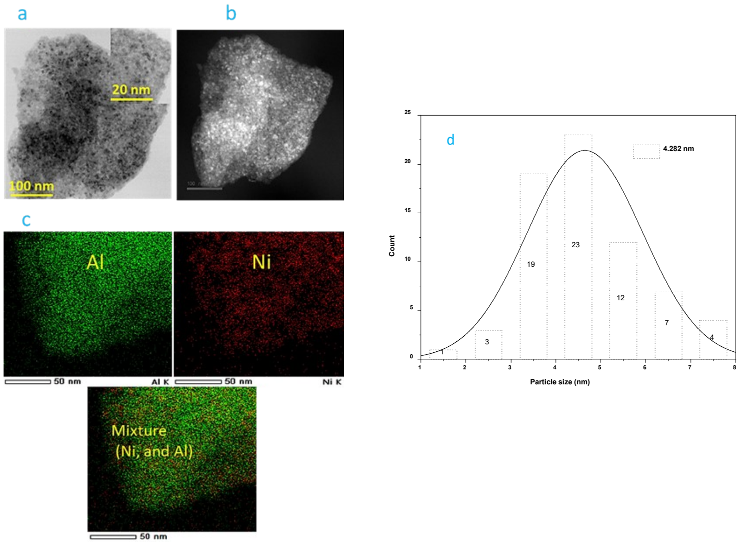

Fig. S6. a) TEM (LM); b) TEM (DM) images; c) elemental mapping; and d) histograms of 5Ni/Al_2O_3 catalyst reduced at 500 °C.

TEM images (Light Mode/Dark Mode), particle size, elemental mapping, and histograms of the prepared 10Ni/Al_2O_3 catalyst are shown in Fig. S7. In TEM images, many darker spots can be observed, identified as Ni particles. Average size of Ni particles was found to be 5.90 nm.

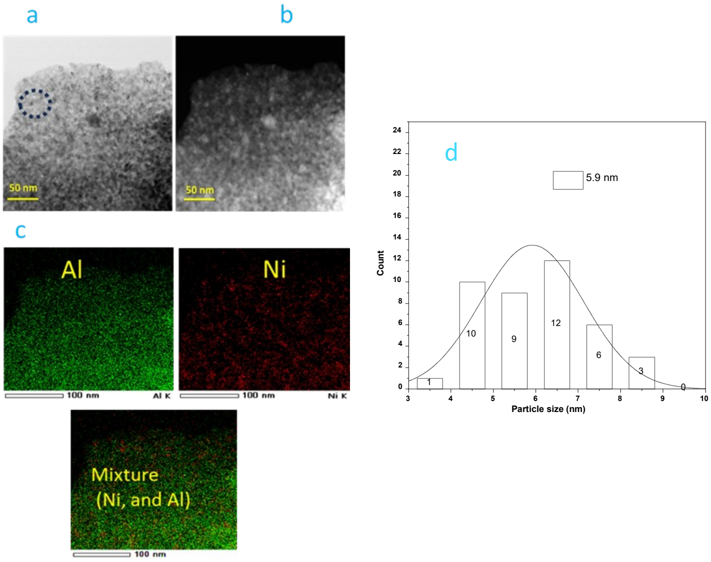

Fig. S7. a) TEM (LM); b) TEM (DM) images; c) elemental mapping; and d) histograms of 5Ni/Al_2O_3 catalyst reduced at 800 °C.

4. Catalytic activity:

Table S1. Reductive depolymerization of polycarbonate (PC) at different reactions temperatures over 66Ni/SiO_2-Al_2O_3 (metal loading in the reaction: 3.33 wt.%)

Entry	Temperature (°C)	X (%)[a]	S_{BPA} (%)
1	200	100	36[b]
2	175	100	34[b]
3	150	81	26[b]
4	125	34	<15[c]

Reaction conditions: 4.6 g of PC in 46 g of THF for 2.5 h with 20 bar of H_2 over 66Ni/SiO_2-Al_2O_3 (metal loading in the reaction: 3.33 wt.%). Number represents the loading of the metal in the catalyst in wt.%. [a] Conversion determined by amount of PC obtained after methanol precipitation. [b] BPA selectivity determined by GC. [c] BPA selectivity determined by GPC.

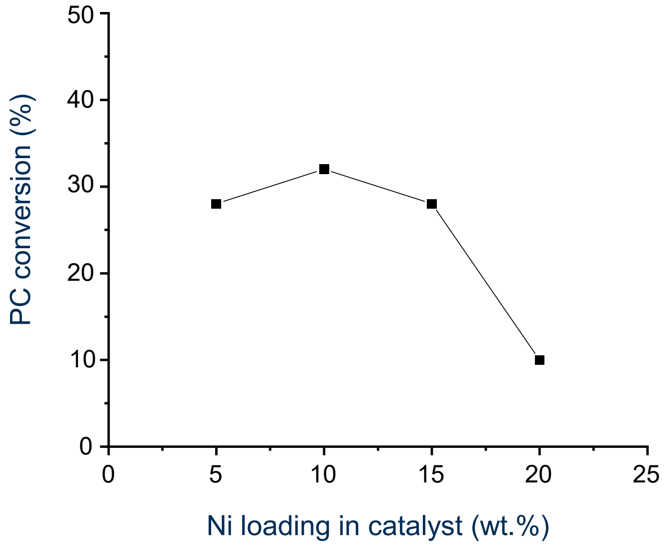

Fig. S8. Effect of the Ni loading in the catalyst in the PC conversion. Reaction conditions: 4.6 g of PC in 46 g of THF at 200 °C for 2.5 h with 20 bar of H_2 over Ni/Al_2O_3 (metal loading in the reaction: 0.25 wt.%).

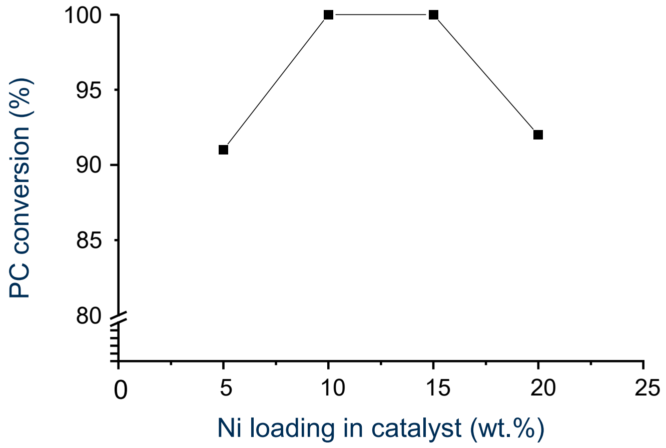

Fig. S9. Effect of the Ni loading in the catalyst in the PC conversion. Reaction conditions: 4.6 g of PC in 46 g of THF at 250 °C for 5 h with 20 bar of H_2 over Ni/Al_2O_3 (metal loading in the reaction: 0.50 wt.%).

Table S2. Reductive depolymerization of polycarbonate (PC) with different Ni/Al_2O_3 catalysts (metal loading in the reaction: 0.50 wt.%)

Entry	Catalyst[a]	X (%)[b]	S_{BPA} (%)[c]	S_{BPA+} (%)[c]	S_{BPA-} (%)[c]	TON (mol/mol)[d]	TOF (h^{-1})[e]
1	$5Ni/Al_2O_3$	91	20	78	2	8.94	1.79
2	$10Ni/Al_2O_3$	100	41	49	10	20.4	4.08
3	$15Ni/Al_2O_3$	100	38	50	12	18.9	3.78
4	$20Ni/Al_2O_3$	91	35	53	12	15.8	3.16

Reaction conditions: 4.6 g of PC in 46 g of THF for 5 h at 250 °C with 20 bar of H_2. [a] Number represents the loading of the metal in the catalyst in wt.%. [b] Conversion determined by amount of PC obtained after methanol precipitation. [c] Selectivity determined by GC. [d] Turnover number (TON) of the catalysts were expressed as mol of BPA produced divided by mol of Ni in the reaction medium. [e] Turnover frequency (TOF) of the catalysts were expressed as mol of BPA produced divided by mol of Ni in the reaction medium per h (determined after 5 h of reaction time).

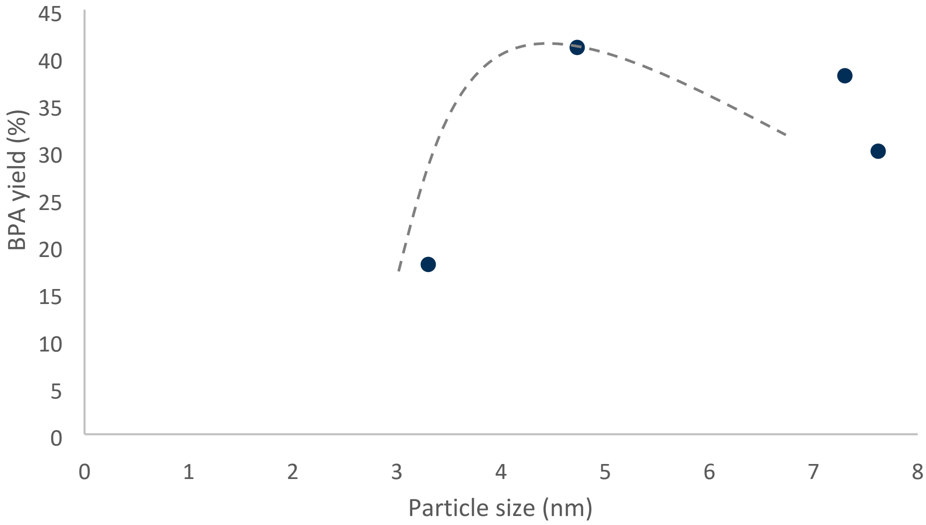

Fig. S10. Effect of the Ni particle size in catalytic activity (BPA yield). Reaction conditions: 4.6 g of PC in 46 g of THF at 250 °C for 5 h with 20 bar of H_2 over Ni/Al_2O_3 (metal loading in the reaction: 0.50 wt.%).

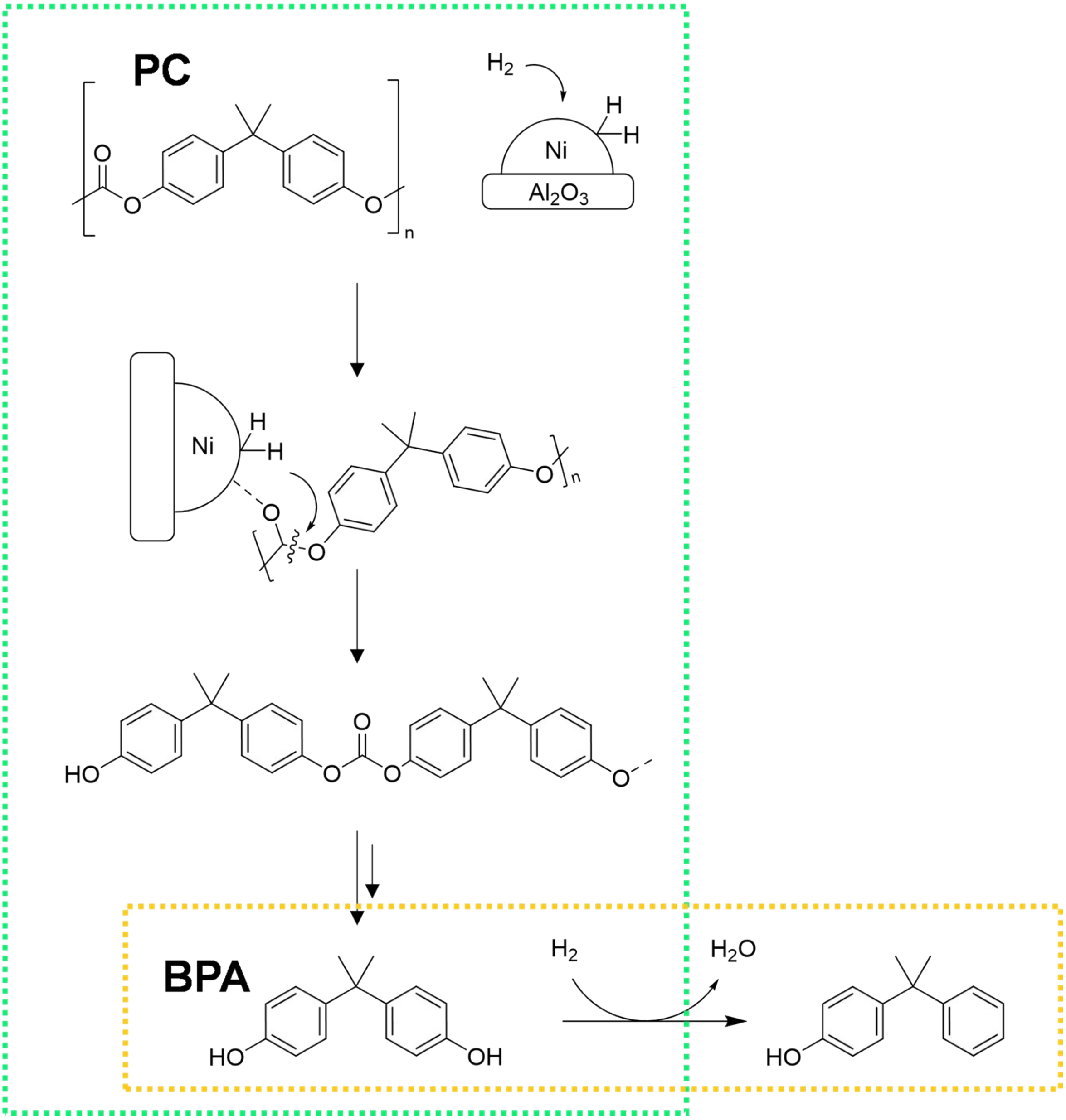

Fig. S11. Potential mechanism for the reductive depolymerization of polycarbonate over Ni/Alumina catalysts to BPA (framed in green) with the decomposition of BPA to 4-cumylphenol (framed in gold).

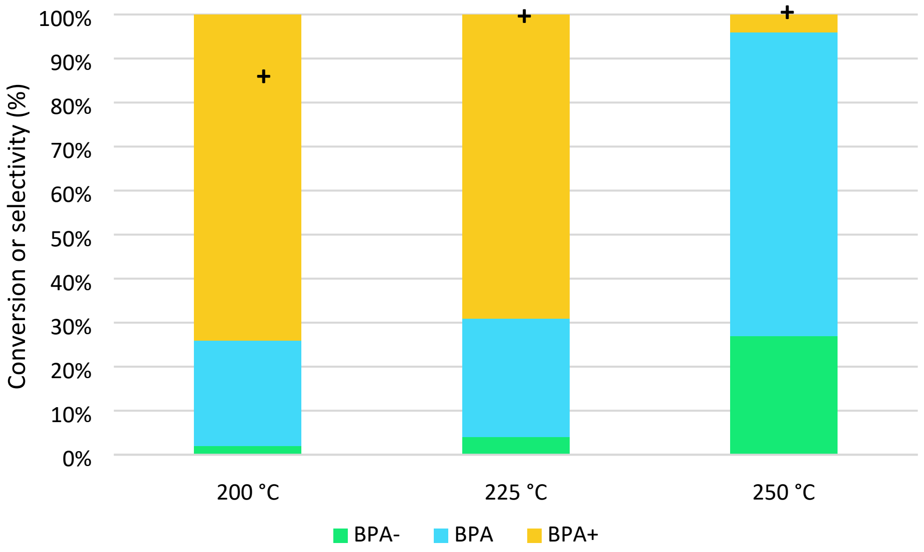

Fig. S12. Effect of temperature on the reductive depolymerization of PC. Conversion indicated by **+**. Reaction conditions: 4.6 g of PC in 46 g of THF for 5 h with 20 bar of H_2 over 10Ni/Al_2O_3 (metal loading in the reaction: 1 wt.%).

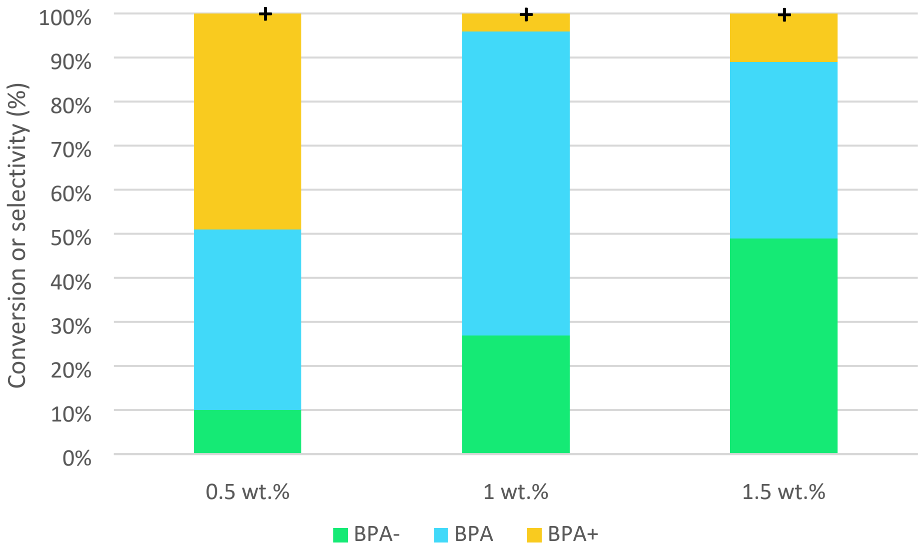

Fig. S13. Effect of Ni loading in the reaction mixture on the reductive depolymerization of PC. Conversion indicated by **+**. Reaction conditions: 4.6 g of PC in 46 g of THF at 250 °C for 5 h with 20 bar of H_2 over 10Ni/Al_2O_3.

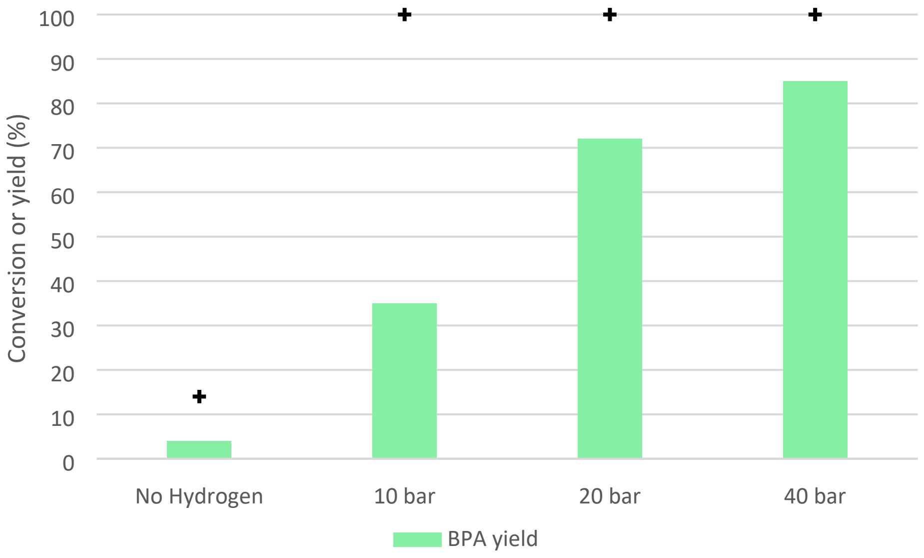

Fig. S14. Effect of hydrogen pressure on the reductive depolymerization of PC. Conversion indicated by **+**. Reaction conditions: 4.6 g of PC in 46 g of THF at 250 °C for 5 h over 10Ni/Al_2O_3 (metal loading in the reaction: 1 wt.%).

Table S3. Solvent screening for the reductive depolymerization of polycarbonate (PC) over 10Ni/Al_2O_3 catalyst (metal loading in the reaction: 1 wt.%).

Solvent	PC conversion (%)	BPA selectivity (%)
THF	100	85
2-MeTHF	100	48
CPME	98	33
Anisole	99	21
Acetone	100	73

Reaction conditions: 4.6 g of PC in 46 g of solvent for 5 h at 250 °C with 40 bar of H_2. Conversion determined by amount of PC obtained after methanol precipitation and BPA selectivity determined by GC.

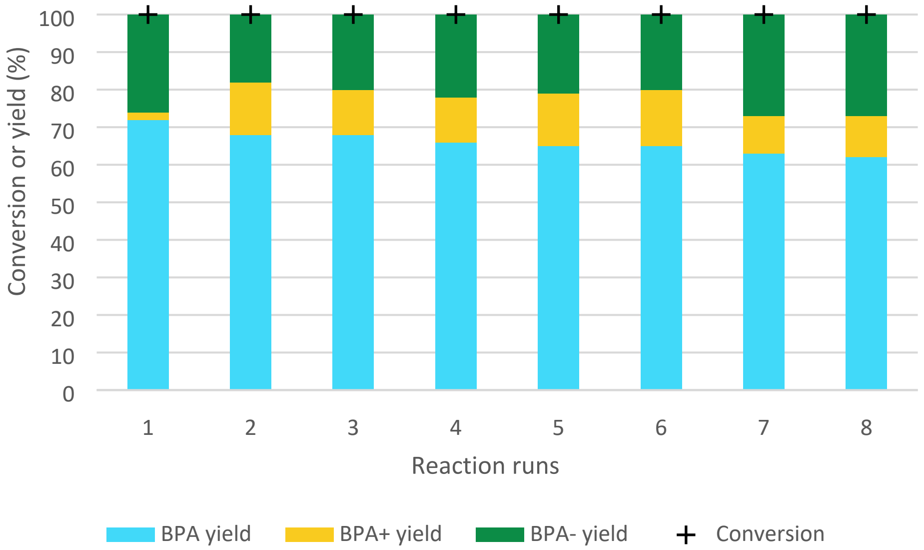

Fig. S15. Recycling tests for the 10Ni/Al_2O_3 catalyst in the reductive depolymerization of PC. Conversion indicated by **+**. Reaction conditions: 4.6 g of PC in 46 g of THF at 250 °C for 5 h over 10Ni/Al_2O_3 (metal loading in the reaction: 1 wt.%). Catalyst reused directly after each reaction cycle after drying overnight at 105 °C.

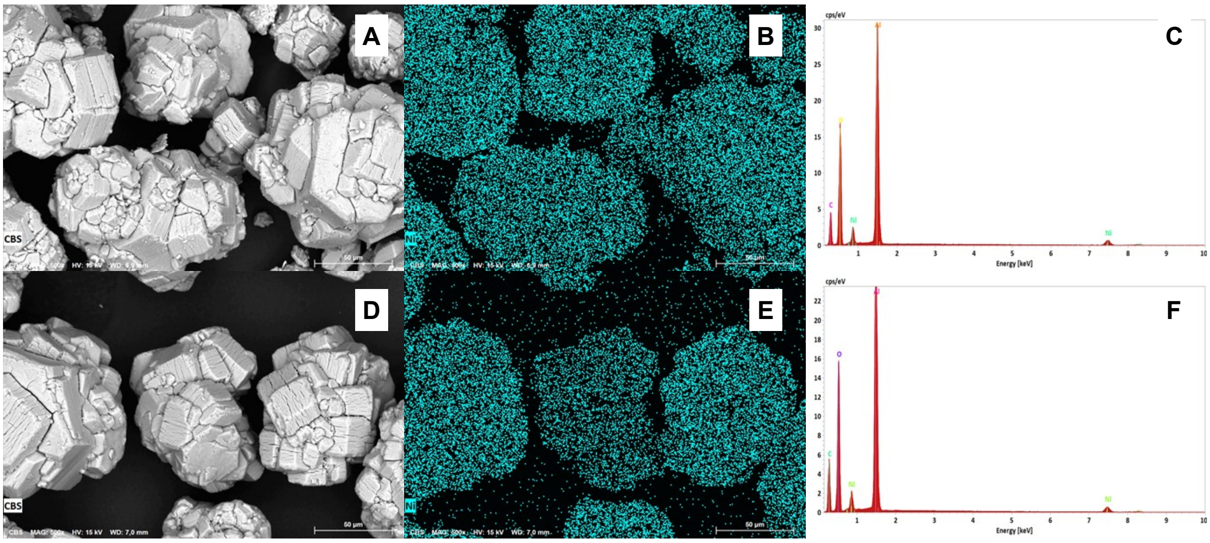

Fig. S16. SEM images, obtained from backscattered electrons (CBS detector) of the sample 10Ni/Al_2O_3 before (A) and after reaction (D); EDS-elemental mapping (Ni) of the sample 10Ni/Al_2O_3 before (B) and after reaction (E); and EDS spectra of the sample 10Ni/Al_2O_3 before (C) and after reaction (F). No differences in Ni loading were observed between the samples (Ni = 10 wt.%), plus the Ni particles seem to be homogenously dispersed on the support (fresh and spent catalyst). Reaction conditions: 4.6 g of PC in 46 g of THF at 250 °C for 5 h with 20 bar of H_2 over 10Ni/Al_2O_3 (metal loading in the reaction: 1 wt.%).

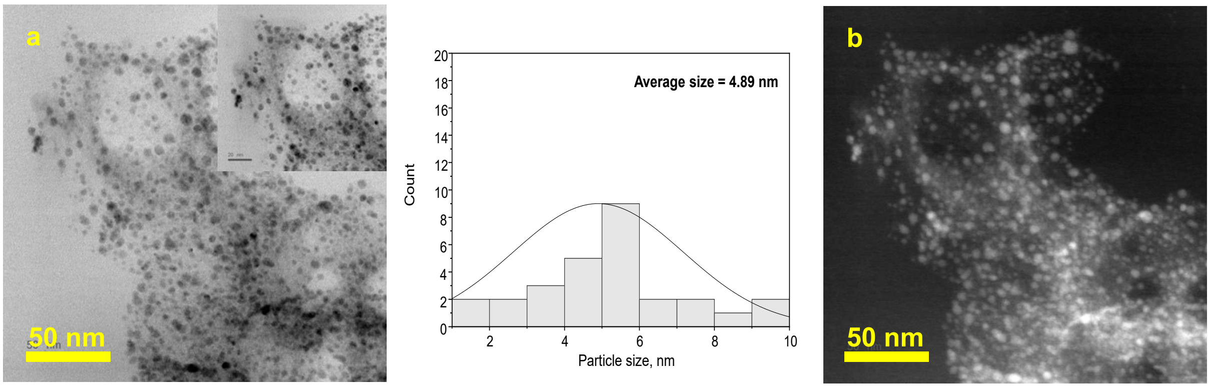

Fig. S17. TEM images of the spent 10Ni/Al_2O_3 catalyst; a) Light Mode, b) Dark Mode. Reaction conditions: 4.6 g of PC in 46 g of THF at 250 °C for 5 h with 20 bar of H_2 over 10Ni/Al_2O_3 (metal loading in the reaction: 1 wt.%). Only a slight increase in particle size is obtained when compared to the fresh catalyst (Fig. 1 in the main text).

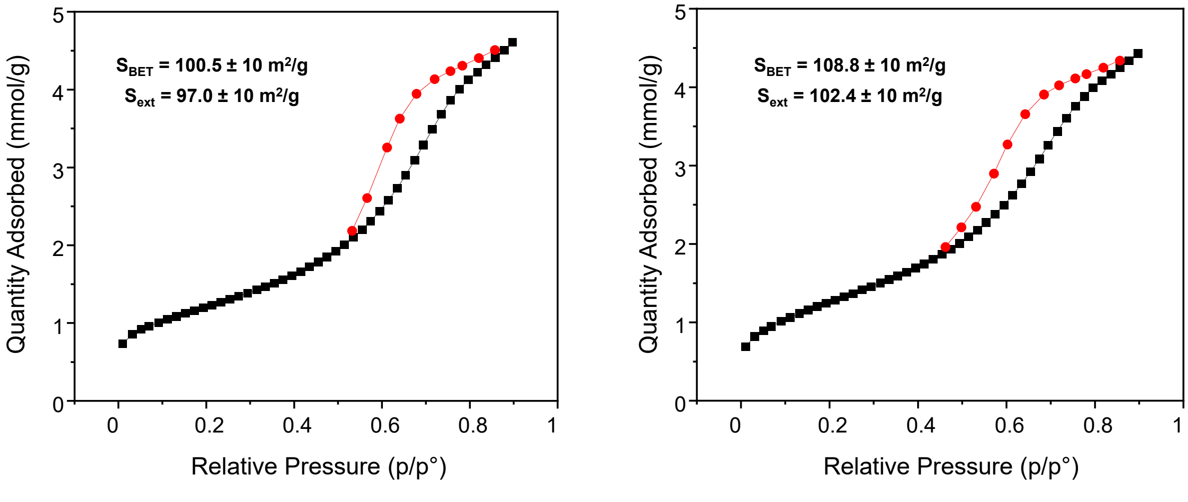

Fig. S18. N_2 physisorption isotherms collected at -196 °C of the catalyst 10Ni/Al2O3 before (left) and after (right) reaction. Reaction conditions: 4.6 g of PC in 46 g of THF at 250 °C for 5 h with 20 bar of H_2 over 10Ni/Al_2O_3 (metal loading in the reaction: 1 wt.%). Textural properties are preserved, both the external and BET area are maintained after the reaction run.

5. Gel permeation Chromatography (GPC):

GPC instrument was equipped with two Styragel HRE4 columns, a refractive index detector (RID-10A), and a UV detector (SPD-20A). Samples were prepared in THF (2 mg/mL) and a flow rate of 0.80 mL/min was used during analysis.

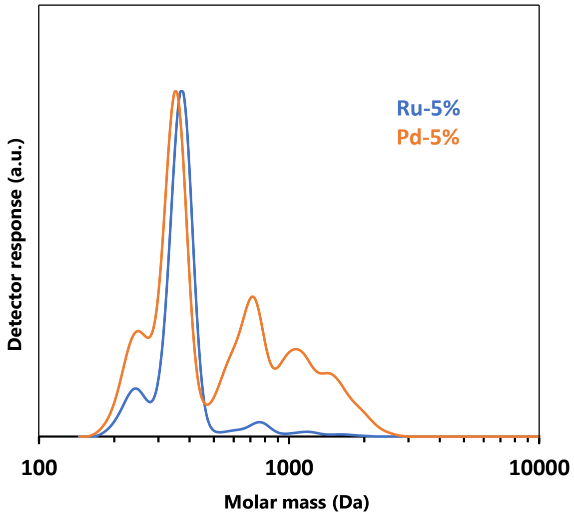

Fig. S19. GPC trace of the filtrate product of the reductive depolymerization of PC over 5Ru/Al_2O_3 and 5Pd/Al_2O_3 (commercial catalyst). Reaction conditions: 4.6 g of PC in 46 g of THF at 200 °C for 2.5 h with 20 bar of H_2 (0.25 wt.% metal loading).

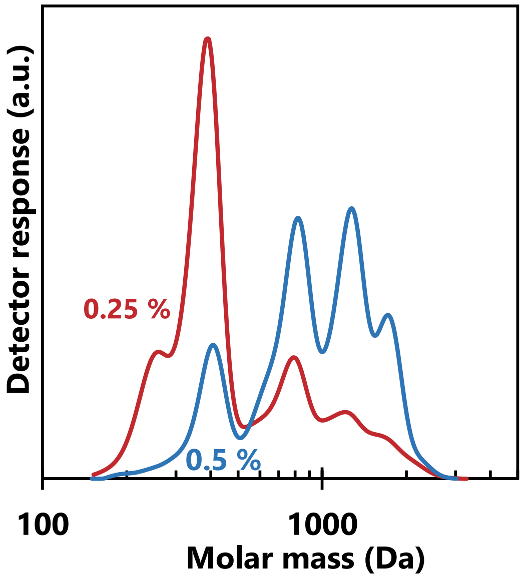

Fig. S20. GPC trace of the filtrate product of the reductive depolymerization of PC over 5NiO/Al_2O_3 catalyst. Reaction conditions: 4.6 g of PC in 46 g of THF at 200 °C for 2.5 h with 20 bar of H_2 (0.25 wt.% or 0.5 wt.% metal loading).

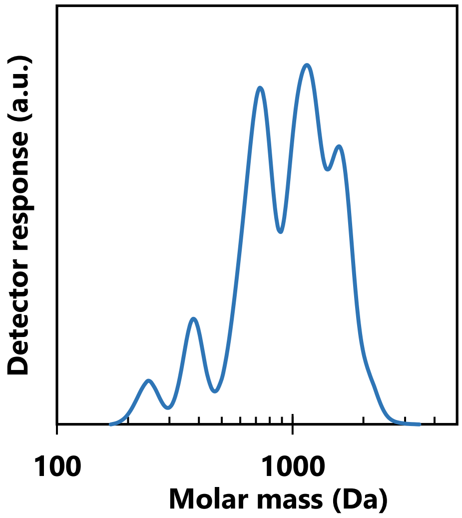

Fig. S21. GPC trace of the filtrate product of the reductive depolymerization of PC over 5Ni/Al_2O_3 (reduced at 800 °C). Reaction conditions: 4.6 g of PC in 46 g of THF at 200 °C for 2.5 h with 20 bar of H_2 (0.25 wt.% metal loading).

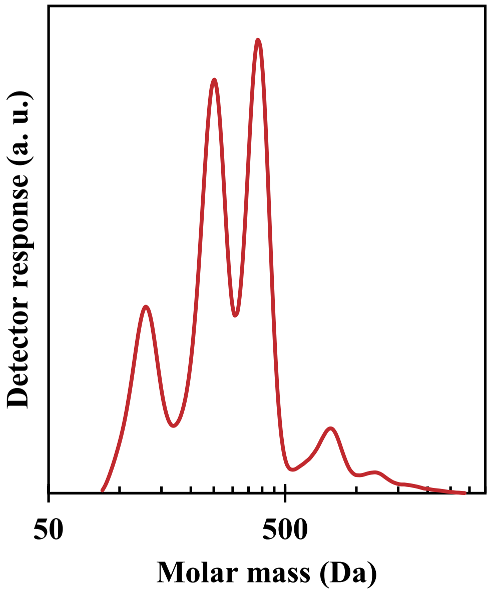

Fig. S22. GPC trace of the filtrate product of the reductive depolymerization of PC over 66Ni/SiO_2-Al_2O_3 (commercial catalyst). Reaction conditions: 4.6 g of PC in 46 g of THF at 200 °C for 2.5 h with 20 bar of H_2 (3.33 wt.% metal loading).

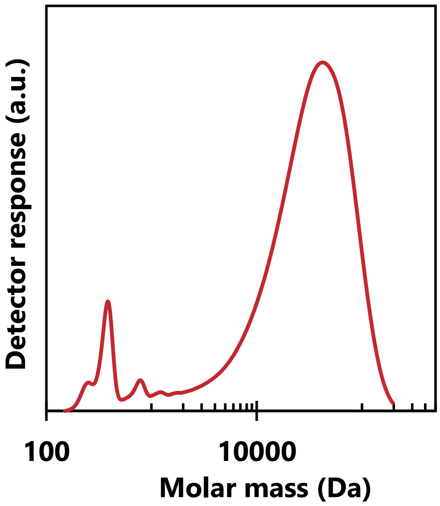

Fig. S23. GPC trace of the filtrate product of the reductive depolymerization of PC over 66Ni/SiO_2-Al_2O_3 (commercial catalyst). Reaction conditions: 4.6 g of PC in 46 g of THF at 200 °C for 2.5 h with 20 bar of H_2 (0.25 wt.% metal loading).

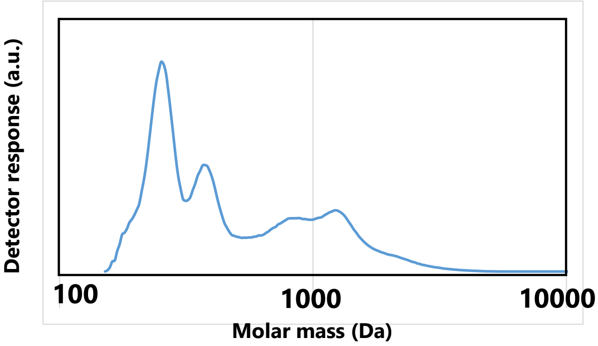

Fig. S24. GPC trace of the filtrate product of the reductive depolymerization of PC over 5Ni/Al_2O_3 (reduced at 500 °C). Reaction conditions: 4.6 g of PC in 46 g of THF at 200 °C for 5 h with 20 bar of H_2 (0.25 wt.% metal loading).