

Ultrasmall amorphous zirconia nanoparticles catalyse polyolefin hydrogenolysis

In the format provided by the
authors and unedited

Table of Contents

Supplementary Methods	2
Supplementary Figures.....	7
Supplementary Tables	79
Supplementary References	88

Supplementary Methods

Chemicals and Materials

All chemicals and starting materials used were commercially obtained and used as received without further purification. 30 nm zirconium oxide (ZrO_2 -30) was purchased from Aldrich. Single-layer graphene oxide (GO, 99 wt.%) was purchased from Cheap Tubes Inc. Zirconium tetrachloride (ZrCl_4 , 99.99%) was purchased from Alfa Aesar. Urea ($\text{CH}_4\text{N}_2\text{O}$, 99%) and sodium hydroxide (98%) were purchased from Fisher Scientific. Tetraethyl orthosilicate (TEOS, 98%), hexadecyltrimethylammonium bromide (CTAB, >98%), ethylenediamine (>99%), hydrochloric acid (35 – 38%, TraceMetal grade), hydrofluoric acid (48 – 51% solution in water, TraceMetal grade), nitric acid (67 – 71%, TraceMetal grade), and polyethylene (PE, $M_n = 20$ kDa, $M_w = 96$ kDa, $D = 4.8$) were purchased from Alfa Aesar. All three inorganic acids are certified to contain less than <1 ppb of Co, Cu, Fe, Ni, Ru, Pd, Pt, Rh, Al, Sb, As, Ba, Be, Bi, Cd, Ca, Ce, Cs, Cr, Dy, Er, Eu, Gd, Ga, Ge, Au, Hf, Ho, In, La, Pb, Li, Lu, Mg, Mn, Hg, Mo, Na, Nd, Nb, K, Pr, Re, Rb, Sm, Sc, Se, Ag, Na, Sr, Ta, Te, Tb, Tl, Th, Tm, Sn, Ti, W, U, V, Yb, Y, Zn, and Zr. The deionized water (DI- H_2O) was generated with a Millipore water purification system (Milli-Q plus) operating at a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ @ 25°C .

Characterization of Catalytic Materials for Comparisons with L-ZrO₂@mSiO₂.

Synthesis of mSiO₂ Platelets. Mesoporous silica platelets (mSiO₂) were prepared following a procedure adapted from the literature.¹ GO (30 mg), CTAB (1.00 g, 2.74 mmol), and sodium hydroxide (0.2 g, 5.0 mmol) were first added into deionized water (DI- H_2O , 45 mL), and then the mixture was subjected to ultrasonication for 3 h. The mixture was heated to 40°C and stirred rapidly for 1 h, and then TEOS (1 mL, 0.94 g, 9.6 mmol) was added in a dropwise fashion to grow mesoporous silica on GO. The reaction mixture was further heated at 40°C for 24 h. The solid product was collected by centrifugation, washed with DI- H_2O (5×50 mL), and washed with ethanol (2×50 mL). The solid product was then redispersed into DI- H_2O , and the above mSiO₂ growth process was repeated 2 times. Finally, the solid product was dried in an oven at 80°C and then calcined at 550°C for 6 h in a box furnace. The final product was then characterized and exhibited a double-layered platelet structure with a narrow empty core.

Synthesis of imp-ZrO₂/mSiO₂. ZrO₂ nanoparticles were deposited throughout the pores and on the external surface of mSiO₂ platelets by the incipient wetness impregnation method. ZrCl₄ (0.044 g) as a methanol solution (0.5 mL) was added in a dropwise manner to the previously prepared mSiO₂ platelets (150 mg) while being mixed by a glass rod. The sample was dried in a laboratory oven at 80 °C and then calcined in a box furnace at 550 °C for 6 h. The final product was characterized by STEM (Supplementary Figure 5), which showed a well-dispersed ZrO₂ throughout imp-ZrO₂/mSiO₂ particles.

Preparation of ZrO₂-6/mSiO₂. ZrO(NO₃)₂·xH₂O (6.374 g) was dissolved in DI-H₂O (15 mL) to form solution A. Urea (10.811 g, 0.18 mol) was dissolved in DI-H₂O (15 mL) to form solution B. Solution A and B were mixed to obtain a solution with the Zr concentration of 0.6 M. The mixture was transferred into a Teflon-lined stainless-steel autoclave and heated at 180 °C for 21 h to give a white crystalline precipitate. The white precipitate was collected, washed with DI-H₂O (2 × 50 mL), and then washed with methanol (2 × 50 mL). The washed sample was redispersed into methanol (38 mL) to obtain suspension C containing ~2.2 g of ZrO₂ nanoparticles. To prepare the ZrO₂-6/mSiO₂ with a ZrO₂ loading of ~5 wt.%, mSiO₂ platelets (50 mg) were mixed with suspension C (35 mg) diluted by methanol (0.25 mL). The mixture was dried in an oven at 60 °C and then calcined at 550 °C for 6 h. The final ZrO₂-6/mSiO₂ product was characterized by STEM (Supplementary Figure 6), which showed that the ZrO₂ nanoparticles are distributed solely on the external surfaces of layered mSiO₂ or are separate aggregates not on the mSiO₂ support.

Synthesis of L-Pt@mSiO₂. The preparation of L-Pt@mSiO₂ followed a modified procedure from the synthesis of L-ZrO₂@mSiO₂. In the first step, urea (0.150 g) was dissolved in DI-H₂O (100 mL), GO (10 mg) was added, and the mixture was treated in an ultrasonication bath for 30 min. Subsequently, an aqueous solution of H₂PtCl₆·6H₂O (0.033 g in 1.25 mL) was added dropwise to the GO suspension, and the mixture was stirred for 3 h at room temperature. The mixture was stirred and heated at 90 °C for 12 h. The solid PtO_{2-x}(OH)_{2x}/GO product was collected by centrifugation, washed with DI-H₂O (3 × 50 mL), and then dispersed into water (10 mL). In the second step, mesoporous silica (mSiO₂) was grown onto PtO_{2-x}(OH)_{2x}/GO following a modified procedure of the one described for the synthesis of L-ZrO₂@mSiO₂, in which PtO_{2-x}(OH)_{2x}/GO (rather than ZrO_{2-x}(OH)_{2x}/GO) was used as the starting materials for the synthesis. Finally, the L-Pt@mSiO₂ product was obtained after calcination at 550 °C for 6 h and characterized by STEM with the particle size of 3.5 ± 0.8 nm (Supplementary Figure 11c). Like the ZrO₂ nanoparticles of

L-ZrO₂@mSiO₂, Pt nanoparticles are localized in the middle of mSiO₂ shells (Supplementary Figure 11a, b).

Characterization of Catalytic Materials

Powder X-ray diffraction (PXRD). The PXRD patterns of ZrO₂-based samples were collected on a Bruker D8 Advance Twin diffractometer (Ni-filtered Cu K α radiation with a wavelength of 1.5406 Å, operated at 40 kV and 40 mA, VANTEC-position-sensitive detector) at a scan speed of 2.0 degrees per min and a step size of 0.02 degrees in 2θ .

Nitrogen gas (N₂) physisorption. The sorption experiments on ZrO₂-based and Pt-containing samples were conducted using a Micromeritics 3Flex surface characterization analyzer at 77 K. The Brunauer-Emmett-Teller (BET) surface area was calculated according to the BET equation, using nitrogen sorption isotherms in the relative pressure range from 0.01 to 0.2. The mesopore size distributions were obtained using BJH method assuming a cylindrical pore model, and the desorption branches of isotherms were used for the calculation.

Inductively coupled plasma mass spectrometry (ICP-MS). The elemental analysis of the ZrO₂ and Pt-based catalysts was carried out on a Thermo Scientific X Series II mass spectrometer. The samples (~1.5 mg) are first treated with hydrofluoric acid (80 μ L) to etch away silica or dissolve the ZrO₂ particles, and then digested with aqua regia (4 mL). The final solutions were diluted with 2.0 v/v % nitric acid to target concentrations for the ICP-MS measurement. The control samples and blanks were treated following the same procedure described above.

Scanning Transmission Electron Microscopy. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy dispersive X-ray spectroscopy (EDX) maps of L-ZrO₂@mSiO₂ were acquired on a FEI Titan Themis 300 probe-corrected scanning transmission electron microscope under 200 kV accelerating voltage. Prior to the imaging, about 1 mg of the ZrO₂-based samples was embedded in 1 mL of Epon epoxy resin and sectioned at 50 nm thickness on a Leica UC6 ultramicrotome with a DiATOME diamond knife.

Solid-State Nuclear Magnetic Resonance Spectroscopy. All solid-state NMR experiments used a Bruker 400 MHz/264 GHz magic angle spinning (MAS) dynamic nuclear polarization (DNP) solid-state (SS)NMR spectrometer equipped with a 3.2 mm low-temperature (100 K) MAS probe, a Bruker AVANCE III console, and a gyrotron microwave source. ZrO₂ and L-

ZrO₂@mSiO₂ samples were impregnated with 16 mM solutions of the TEKPol² bisnitroxide polarizing agent³ in deuterated 1,1,2,2-tetrachloroethane and packed into 3.2 mm sapphire rotors. To reach the positive ¹⁷O direct DNP condition,⁴ the field of the NMR magnet was decreased by 500 ppm, relative to the field which yields the ¹H positive DNP maximum when using nitroxide polarizing agents. Unless otherwise stated, all experiments were conducted at a MAS rate of 12.5 kHz. A 25 kHz effective central transition (CT)-selective radiofrequency (rf) field was used for all ¹⁷O pulses and all experiments utilized high-power ¹H decoupling. ¹⁷O{¹H} phase-shifting effects a smooth transfer of polarization (PRESTO) experiments⁵⁻⁷ utilized two rotor periods of R18⁷ recoupling.⁸ A QCPMG spikelet separation of 625 Hz was used, and 30 echoes were acquired.

All ZrO₂ samples were moderately (ca. <20 %) enriched in ¹⁷O to enhance sensitivity. Samples were first heated to ca. 430 °C under dynamic vacuum for approximately 8 h to remove surface hydroxyl species. After cooling to room temperature, the samples were treated with minimal amounts of 40% H₂¹⁷O (Cortecnet) under a nitrogen atmosphere and left to react overnight. Samples were then dried *in vacuo* at room temperature for approximately 8 h.

X-ray Absorption Spectroscopy (XAS). The X-ray absorption spectroscopy measurements at the Zr K-edge (17998 eV) on L-ZrO₂@mSiO₂ were performed at the Advanced Photon Source (APS) on the bending-magnet beamline 12-BM and 20-BM. A Zr metal foil was used to calibrate the X-ray beam energy and was simultaneously measured with each sample. For each sample, several scans were taken and averaged to gain a better signal-to-noise ratio. The radiation was monochromatized by a Si (111) double-crystal monochromator. The harmonic rejection was accomplished with a Harmonic rejection mirror. The XANES spectroscopy was collected in both transmission and fluorescence mode. And the standards (including the foil) have been measured in transmission mode. XAS data reduction and analysis were processed by Athena software.

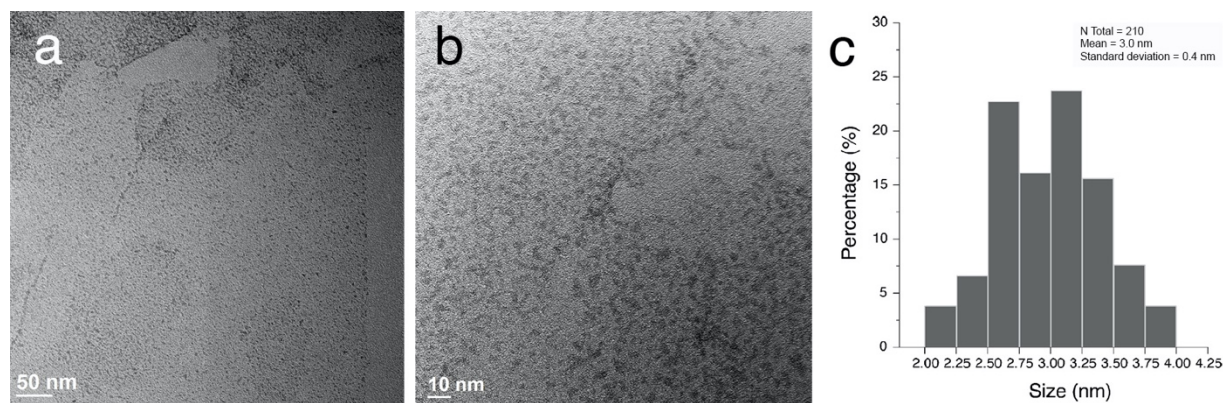
Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Infrared (IR) spectroscopy on L-ZrO₂@mSiO₂ was carried out on a Nicolet iS50 FTIR instrument with an MCT-B detector, and a Praying Mantis diffuse reflectance accessory and a high temperature reaction chamber from Harrick Scientific. IR spectra were collected with a resolution of 4 cm⁻¹. An average of 64 spectra was used for the reported spectra.

A custom-built gas manifold with carefully calibrated mass flow controllers was employed for delivering purge (Ar, Airgas UHP grade) and reactive (H₂, Airgas UHP grade; D₂ Aldrich 99.8% D) gases. He and H₂ gases were further dried by passing them through Restek indicating

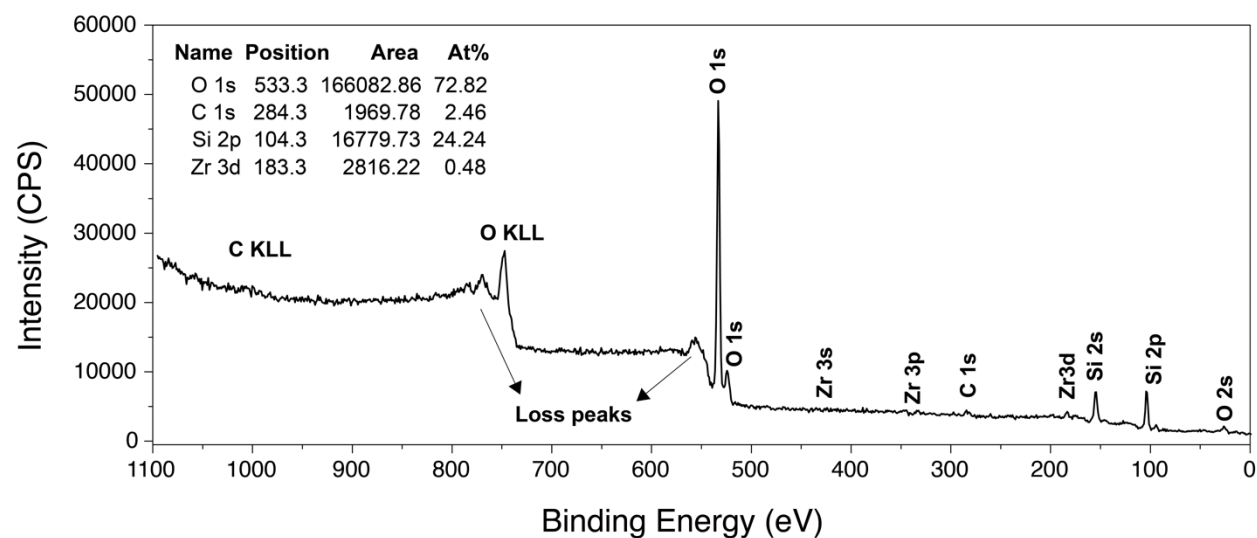
purifying columns (model #22020). Both the gas manifold and reaction chamber were gas-tight and were checked for leaks prior to the experiments (leak rates better than 10^{-5} Pa·L/s at all connections).

Briefly, L-ZrO₂@mSiO₂ and ZrO₂-6/mSiO₂ samples were activated by reduction at 550 °C for 3 h in a 3:1 mixture of H₂ in Ar flowing at 40 mL/min. Samples were then cooled to 300 °C in flowing Ar. The spectra were acquired at 300 °C in pure H₂ (or D₂) flowing at 30 mL/min.

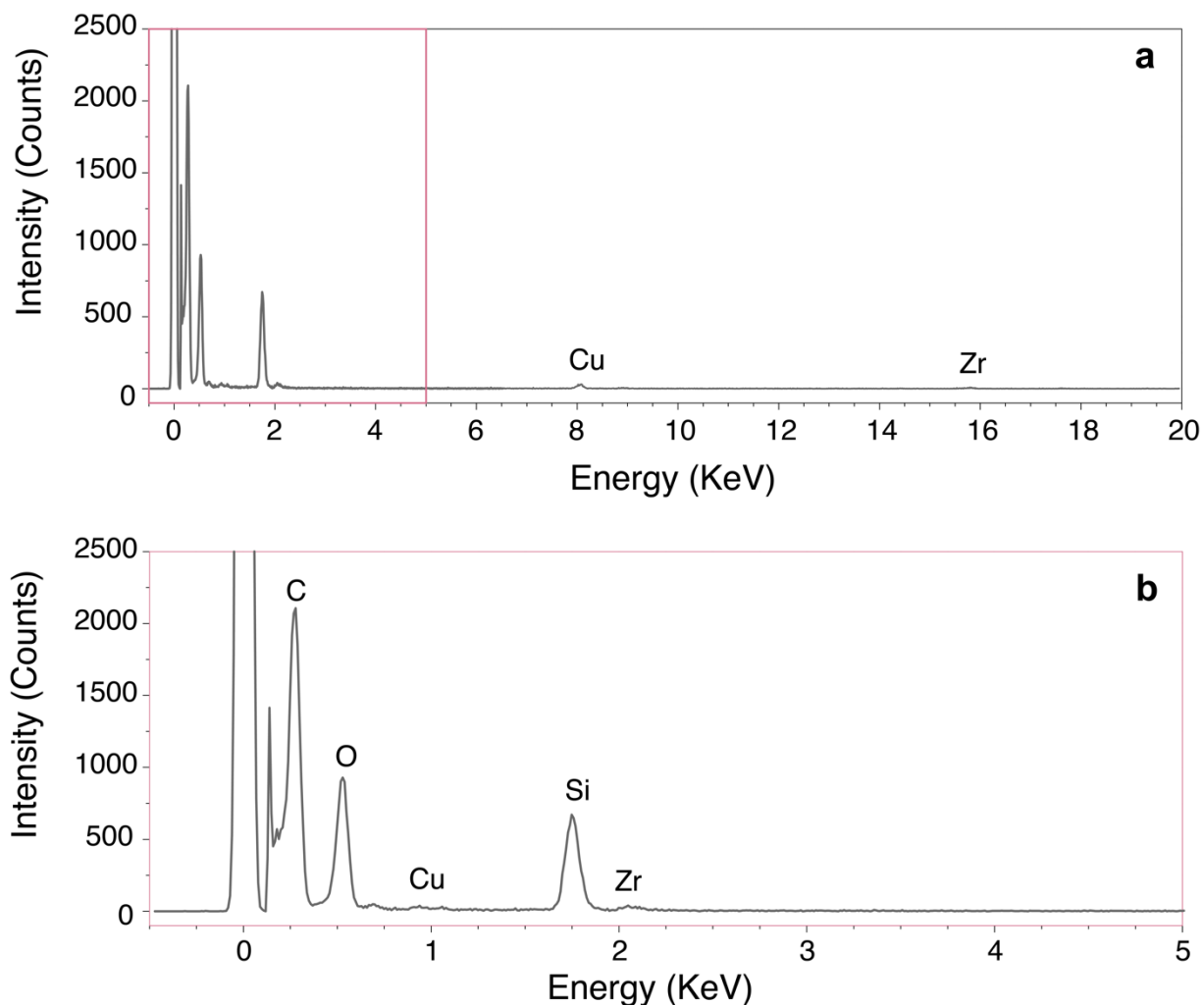
Supplementary Figures



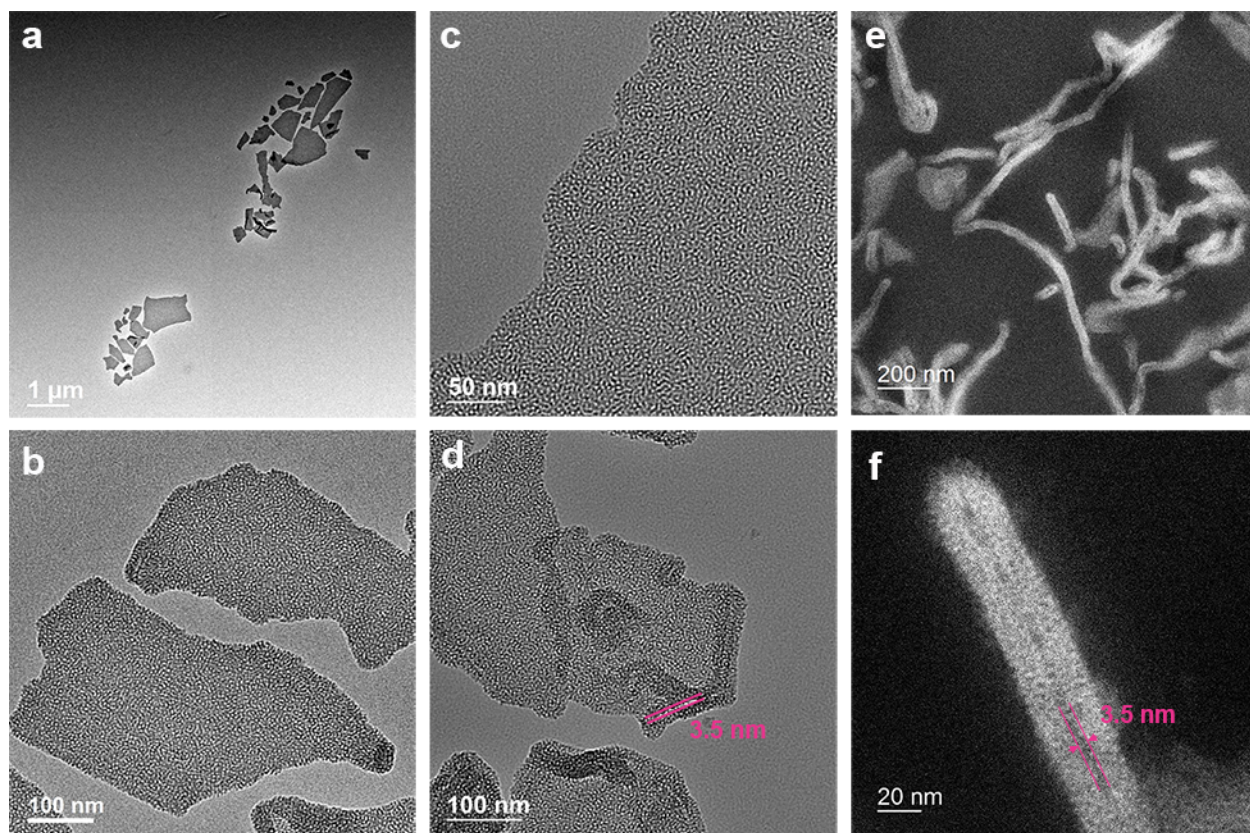
Supplementary Figure 1. a) Low- and b) high-magnification TEM images of the $\text{ZrO}_x(\text{OH})_{4-2x}/\text{GO}$. c) Size distribution of $\text{ZrO}_x(\text{OH})_{4-2x}$ nanoparticles on GO with average size of 3.0 ± 0.4 nm.



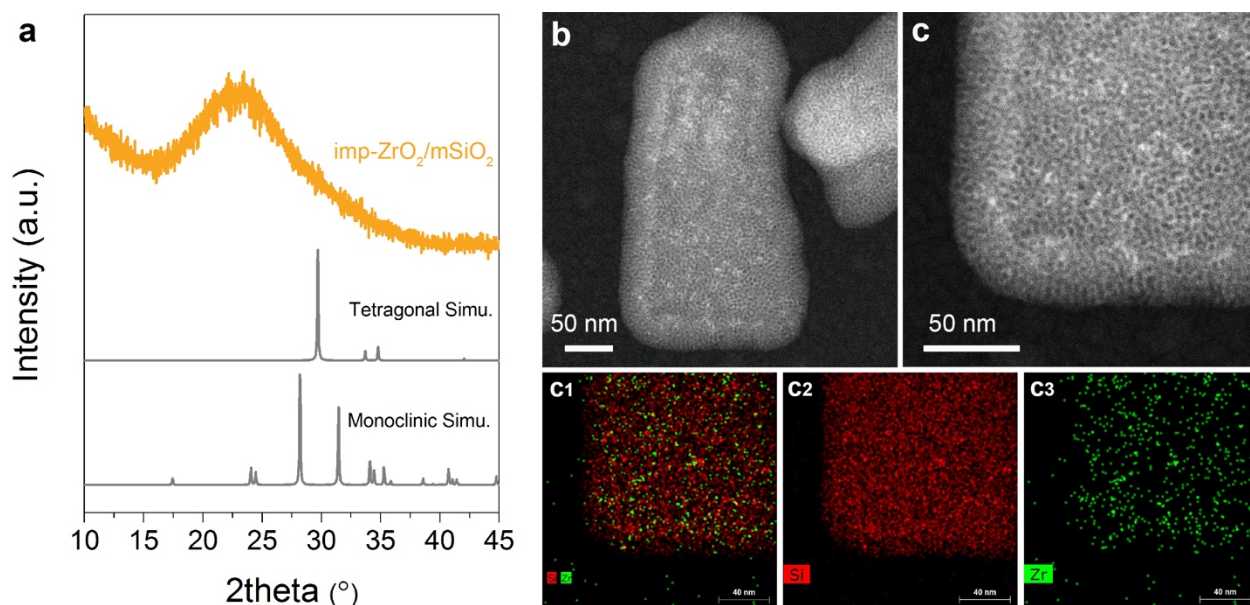
Supplementary Figure 2. X-ray photoelectron spectroscopy (XPS) survey spectrum (1100 – 0 eV) of L-ZrO₂@mSiO₂ and the peak assignments. As shown in the spectrum, within the XPS detection limit (0.1 at.%), only O, C, Si, and Zr were detected with the loading of 72.82 at.%, 2.46 at.%, 24.24 at.%, and 0.48 at.%, respectively.



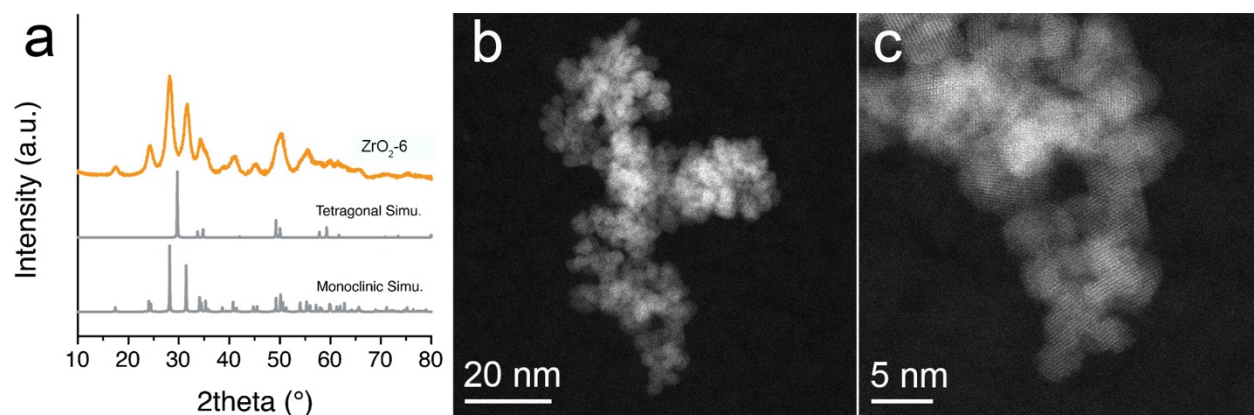
Supplementary Figure 3. a) STEM-EDX spectrum (-0.5 – 20.0 KeV) and b) enlarged spectrum (-0.5 – 5.0 KeV) of L-ZrO₂@mSiO₂. Apart from the C, O, Si, Zr, and Cu species, other metal impurities were not detected. Note that the detected C and Cu signals could be only contributed by the TEM Cu grid with coated carbon thin film.



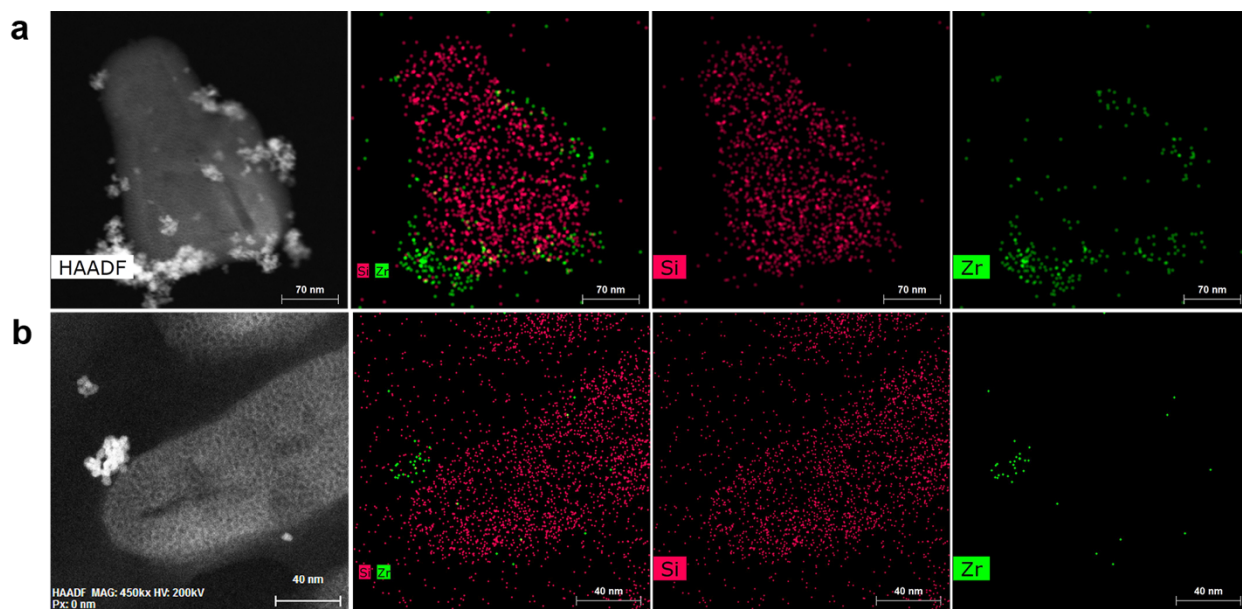
Supplementary Figure 4. TEM images of GO@mSiO₂ nanoplatelets a, b) before and c, d) after removal of GO and CTAB by calcination at 550 °C for 6 h. e) Low- and f) high-magnification STEM images of cross-sectioned mSiO₂ nanoplatelets embedded in epoxy resin. a) low-magnification TEM image shows a good dispersity of GO@mSiO₂ nanoplatelets; b) high-magnification TEM image shows the silica shell is mesoporous; c) displays that mSiO₂ retained the mesoporous structure after calcination. A narrow (~3.5 nm) bright/dark band is observed in d)/f), suggesting a narrow open cavity between two mSiO₂ layers.



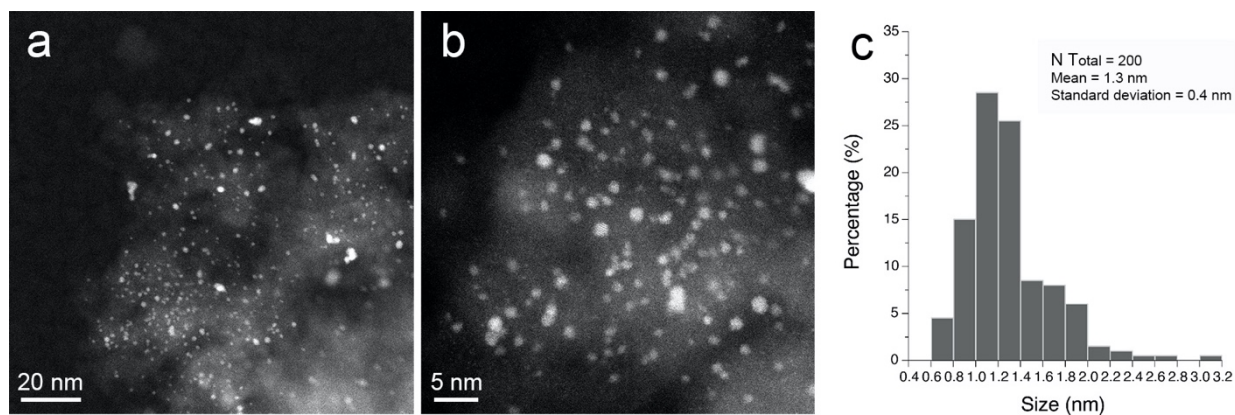
Supplementary Figure 5. a) PXRD pattern, b, c) HAADF STEM images, and c1–c3) energy dispersive X-ray spectroscopy (EDX) elemental maps of imp-ZrO₂/mSiO₂ sample. PXRD pattern shows a featureless broad hump, indicating imp-ZrO₂/mSiO₂ is an amorphous material. The STEM image and the EDX elemental maps display an even distribution of ZrO₂ onto the layered mSiO₂ support.



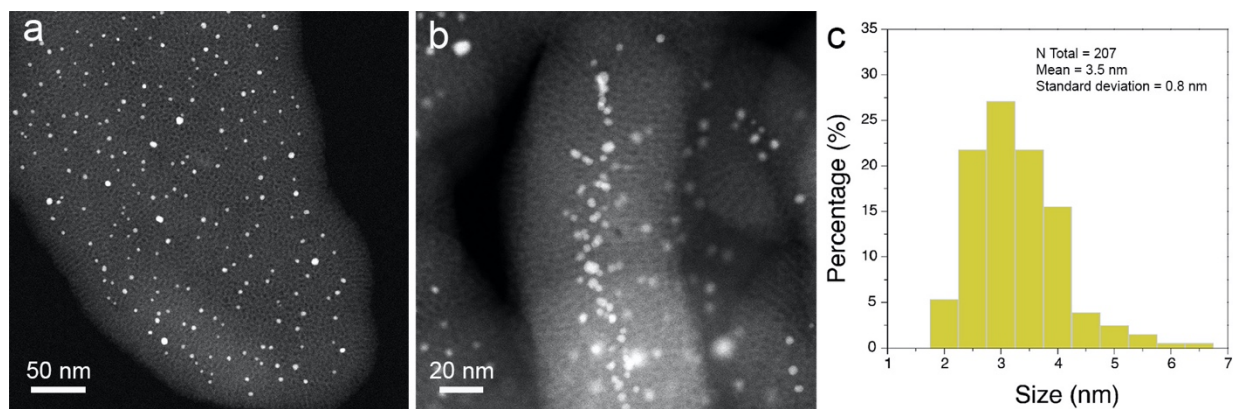
Supplementary Figure 6. a) PXRD pattern of ZrO₂-6 obtained from a hydrothermal synthesis, together with the simulated patterns of crystalline ZrO₂ with tetragonal and monoclinic phases. The pattern shows that ZrO₂-6 is monoclinic with an average size of 6.4 nm, estimated by the Scherrer equation: $L = 0.94\lambda / (\cos\theta \cdot B)$, where L is mean particle size, B is the peak broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening (an empirical value 0.1° in 2θ is used). The full widths at half maximum (FWHM) of the ($\bar{1}11$) peak (1.388°) and the (111) peak (1.400°) were used for the mean size estimation. b) The low-magnification STEM image shows that ZrO₂ nanoparticles are nano-agglomerates with the primary size less than 6 nm and c) high-magnification STEM image shows lattice fringes at nanoparticles, indicative of the crystalline characteristics of nanoparticles.



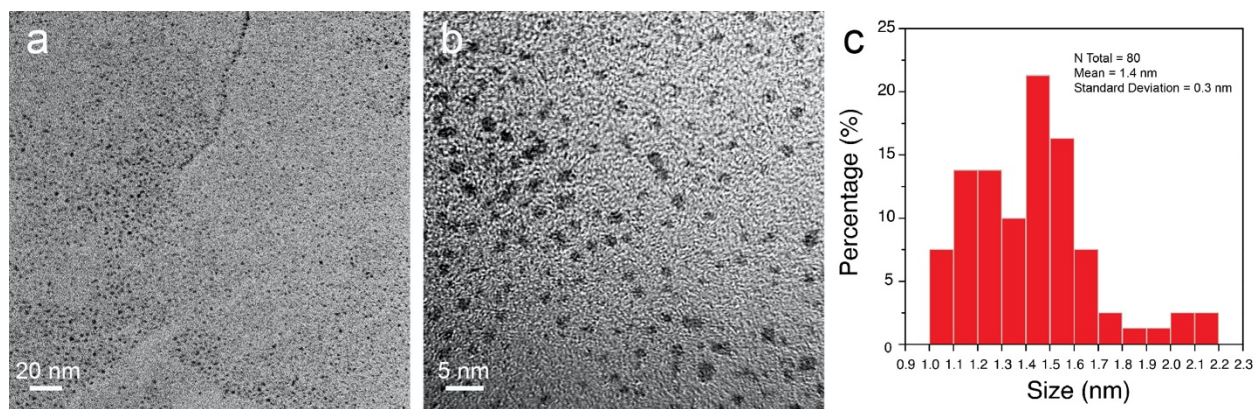
Supplementary Figure 7. a) A HAADF image and the corresponding EDX elemental maps (left – right: Si and Zr mix, Si, Zr) of ZrO₂-6/mSiO₂. b) A HAADF image and the corresponding EDX elemental maps (left – right: Si and Zr mix, Si, Zr) of a cross-sectioned ZrO₂-6/mSiO₂ particle. The top-down and cross-section view STEM images show that brighter contrast only exist on the external surface of mSiO₂ platelets. The corresponding elemental maps display that Zr are solely distributed on the external surfaces. Taken together, ZrO₂ nanoparticles are confirmed distributed on the external surfaces on mSiO₂ particles or as separate aggregates not on mSiO₂.



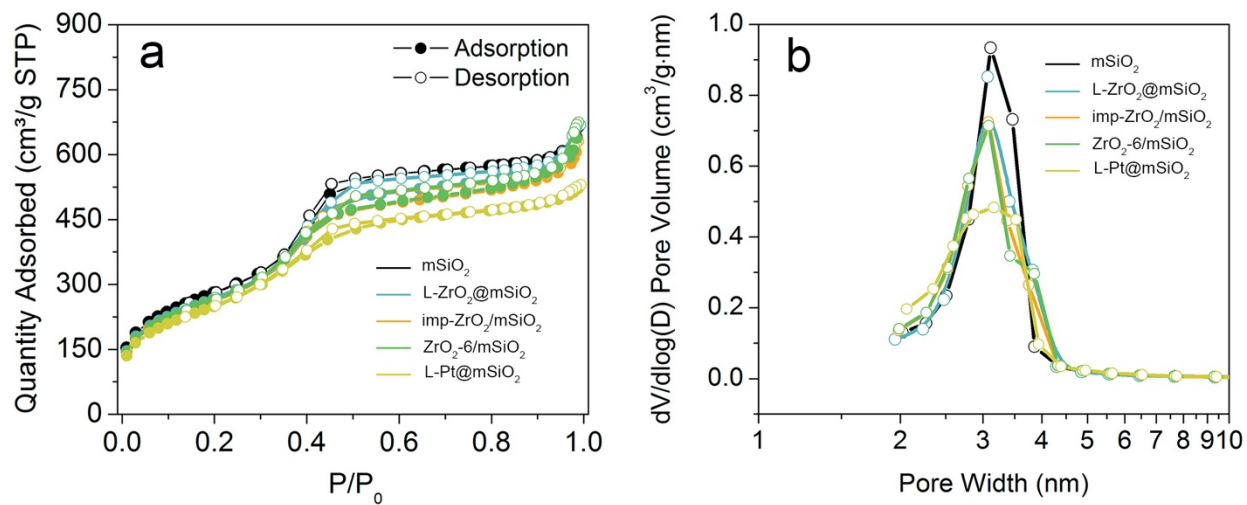
Supplementary Figure 8. a) Low-magnification and b) high-magnification HAADF STEM images of commercial Pt/C catalyst from Alfa Aesar. c) Size distribution of Pt nanoparticles of Pt/C catalyst with the average size of 1.3 ± 0.4 nm.



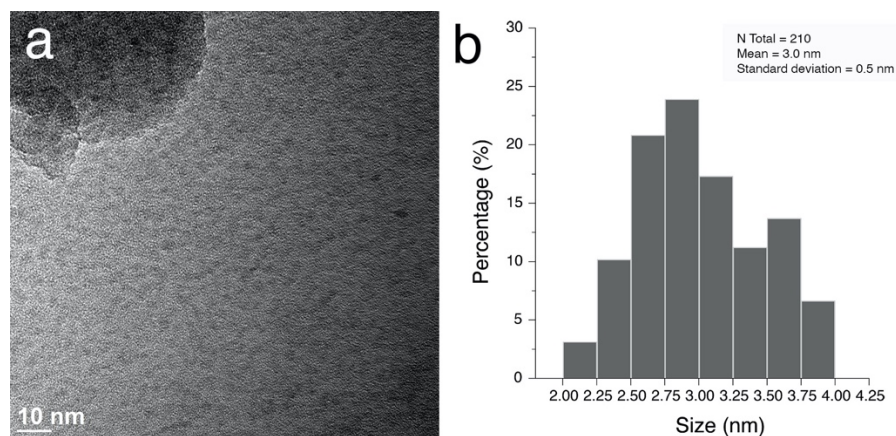
Supplementary Figure 9. HAADF STEM images of L-Pt@mSiO₂ catalyst from a) top-down view and b) side view. c) Size distribution of Pt nanoparticles of L-Pt@mSiO₂ catalyst with the average size of 3.5 ± 0.8 nm.



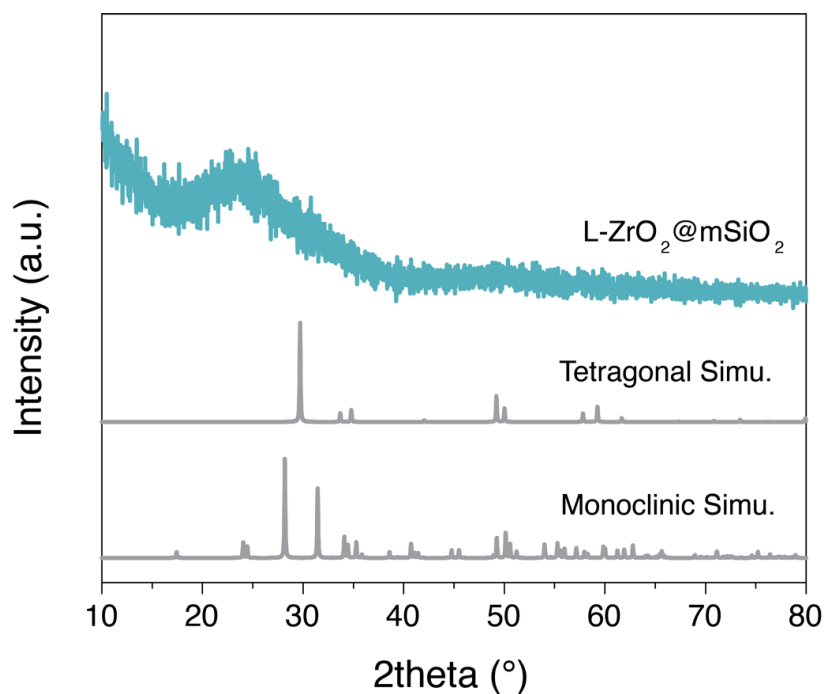
Supplementary Figure 10. a) Low- and b) high-magnification TEM images of the $\text{PtO}_x(\text{OH})_{4-2x}/\text{GO}$ composite. c) Size distribution of $\text{PtO}_x(\text{OH})_{4-2x}$ nanoparticles on GO.



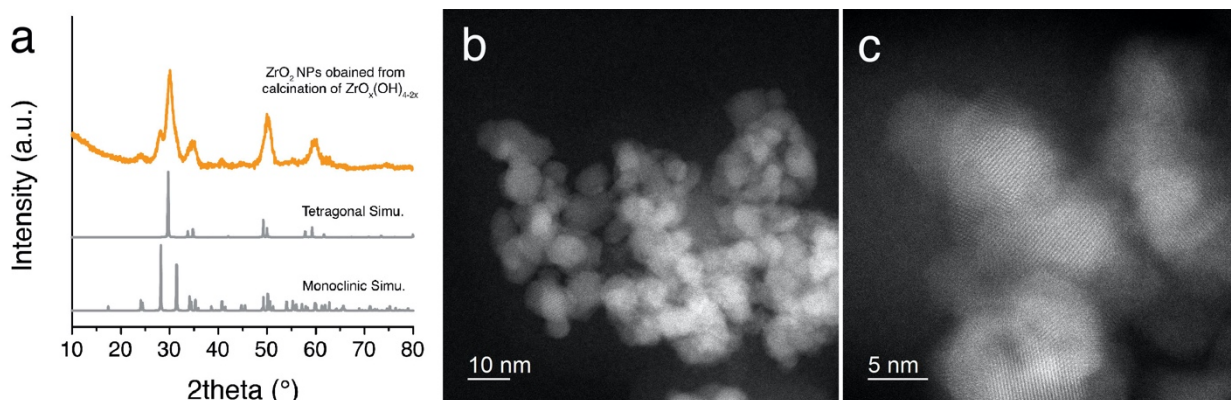
Supplementary Figure 11. a) N₂ sorption isotherms and b) BJH Pore size distributions of the mSiO₂, L-ZrO₂@mSiO₂, imp-ZrO₂@mSiO₂, ZrO₂-6/mSiO₂, and L-Pt@mSiO₂.



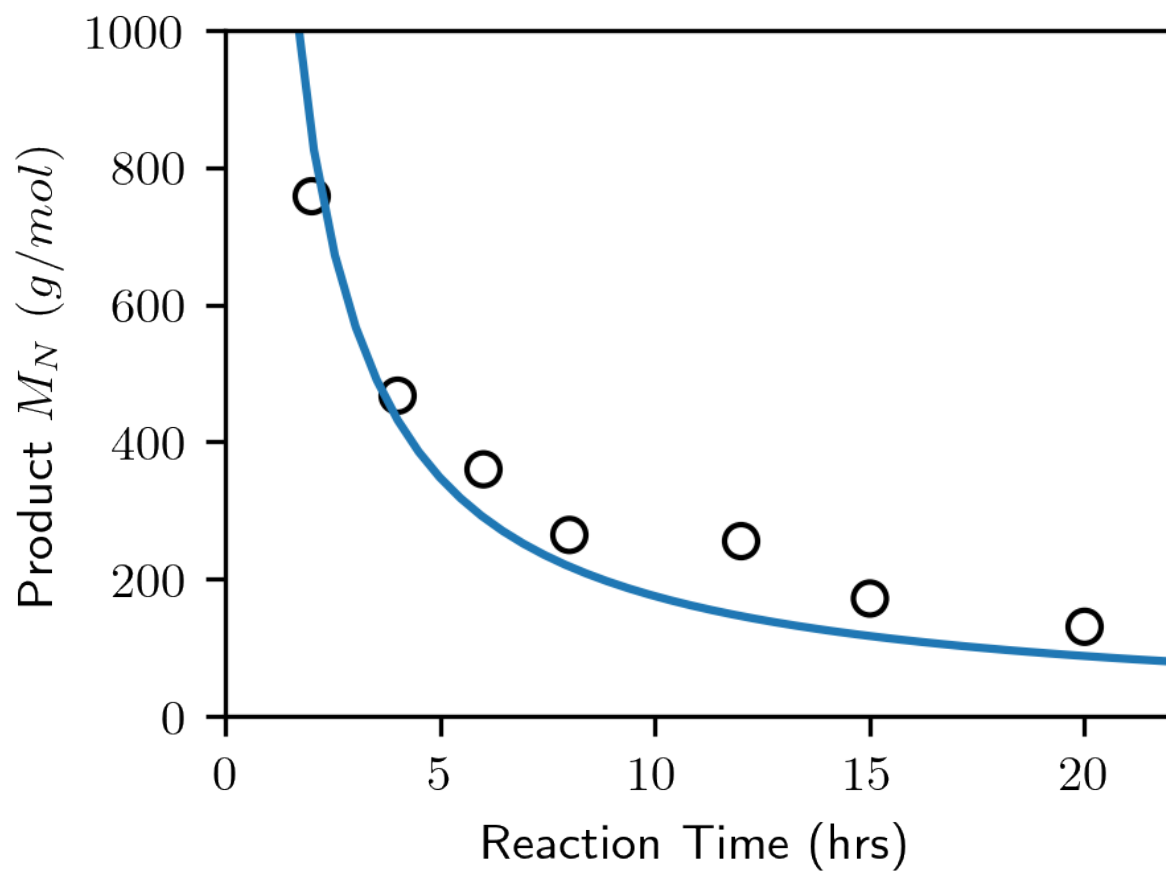
Supplementary Figure 12. a) TEM image of L-ZrO₂@mSiO₂ with the electron beam focused on ZrO₂ nanoparticles and b) size distribution of ZrO₂ nanoparticles on L-ZrO₂@mSiO₂ with the average size of 3.0 ± 0.5 nm.



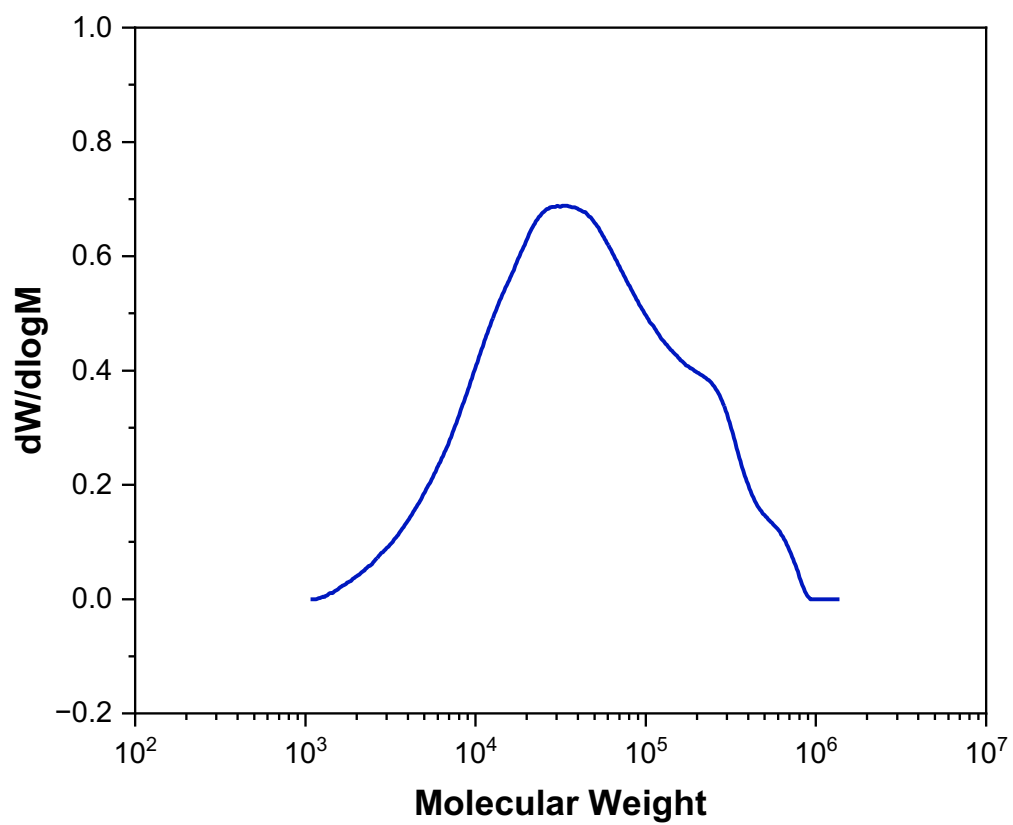
Supplementary Figure 13. Powder X-ray Diffraction (PXRD) pattern of L-ZrO₂@mSiO₂ sample, together with the simulated patterns of crystalline ZrO₂ with tetragonal and monoclinic phases. The broad hump in the pattern of L-ZrO₂@mSiO₂ indicates the amorphous characteristics of the sample.



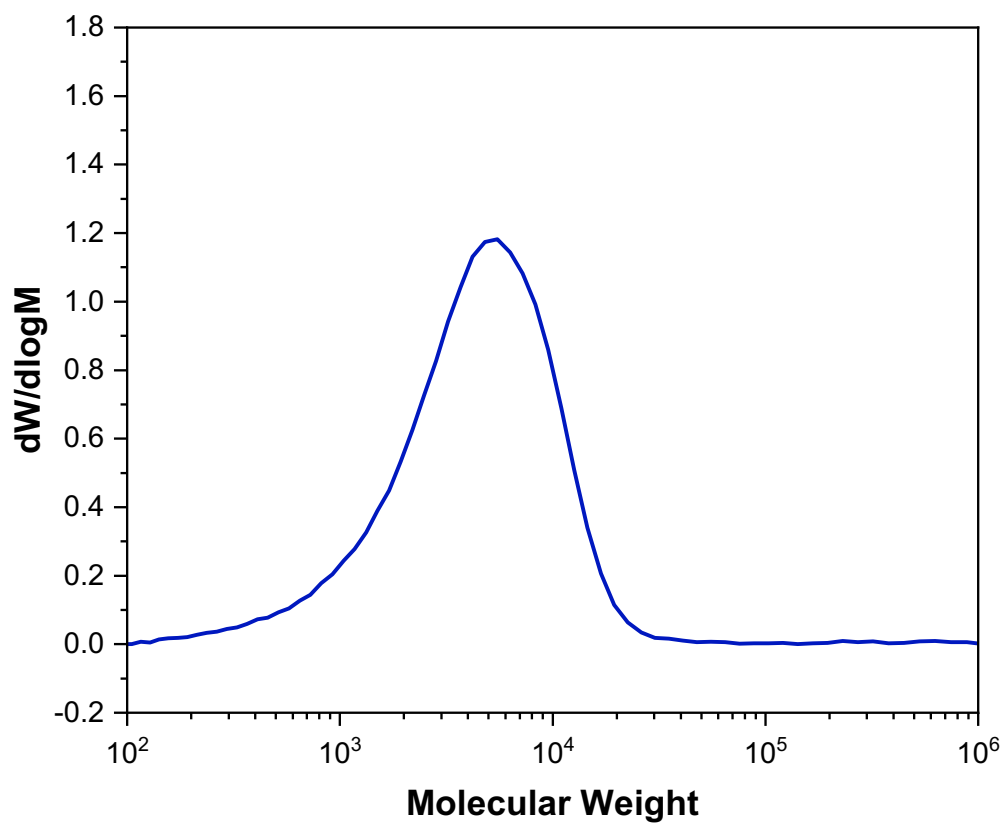
Supplementary Figure 14. a) PXRD pattern of the sample of ZrO₂ nanoparticles obtained from the calcination of ZrO_x(OH)_{4-2x}/GO composite at 550 °C for 6 h, together with the simulated patterns of crystalline ZrO₂ with tetragonal and monoclinic phases. The pattern shows the ZrO₂ nanoparticles contain both tetragonal and monoclinic nanocrystallites with a size of 5.5 nm and 9.3 nm, respectively, estimated by the Scherrer equation: $L = 0.94\lambda / (\cos\theta \cdot B)$, where L is mean particle size, B is the peak broadening defined by FWHM, after subtracting the instrumental line broadening (an empirical value 0.1° in 2θ is used). The FWHM of the (101) peak (1.605°) for the tetragonal phase and the (10 $\bar{1}$) peak (0.984°) for the monoclinic phase are used for the mean size estimation. b) low-magnification HAADF STEM image displays that ZrO₂ nanoparticles are nano-agglomerates with the primary size less than 10 nm and c) high-magnification STEM image shows that lattice fringes at nanoparticles, indicating the crystalline characteristics of nanoparticles.



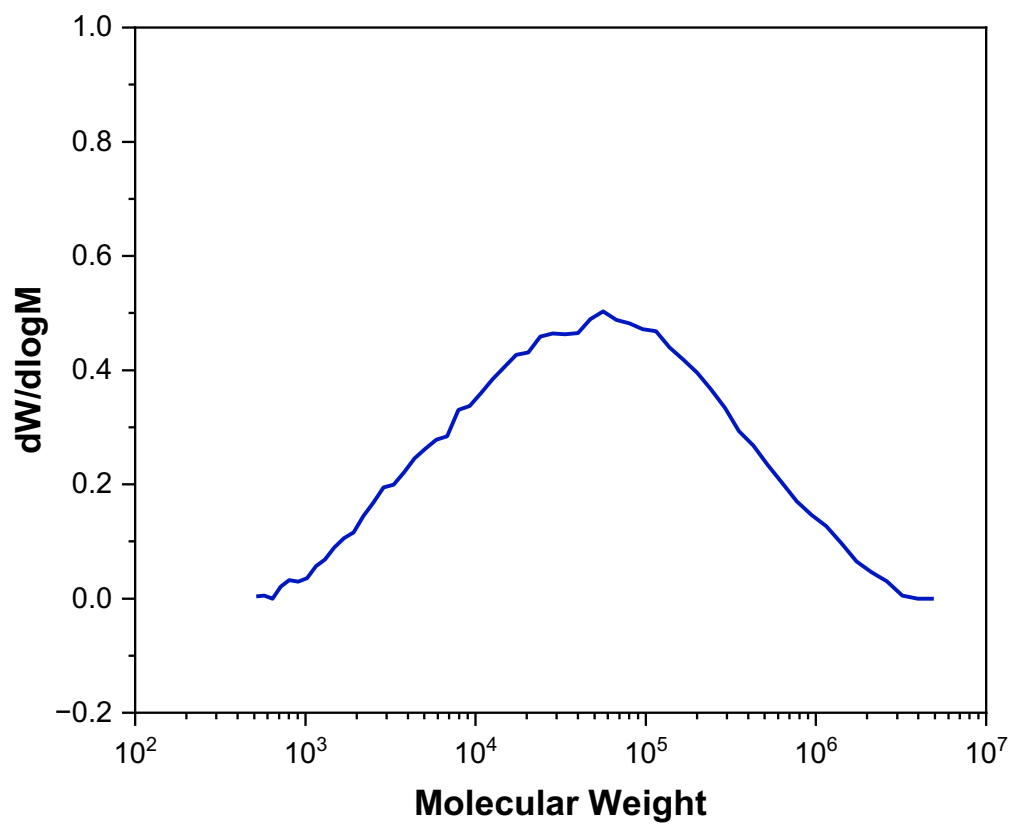
Supplementary Figure 15. Experimental M_n of the lumped phases fitted to eq 3.



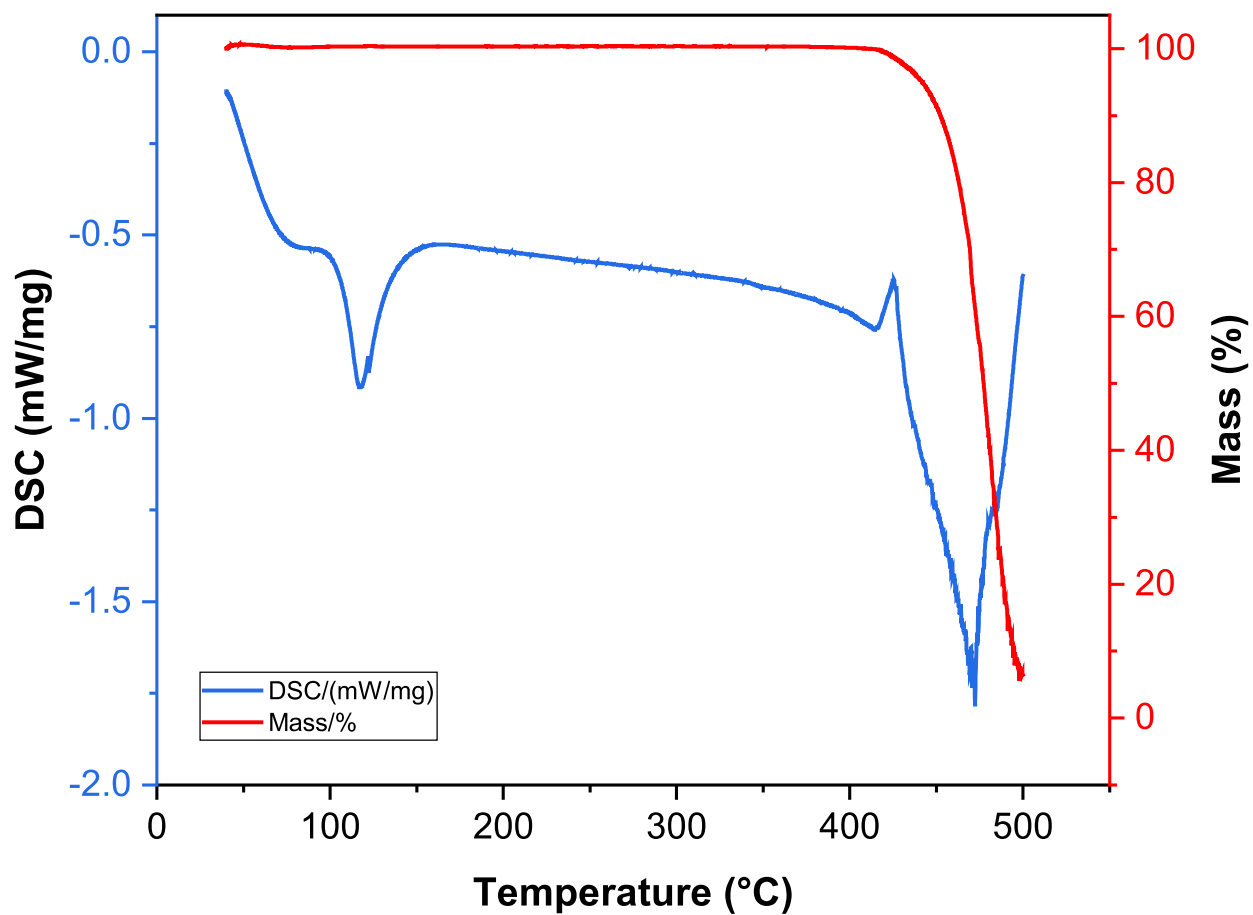
Supplementary Figure 16. GPC analysis of molecular mass and distribution of the commercial PE starting material; $M_n = 20$ kDa, $M_w = 90$ kDa (Alfa Aesar 42607).



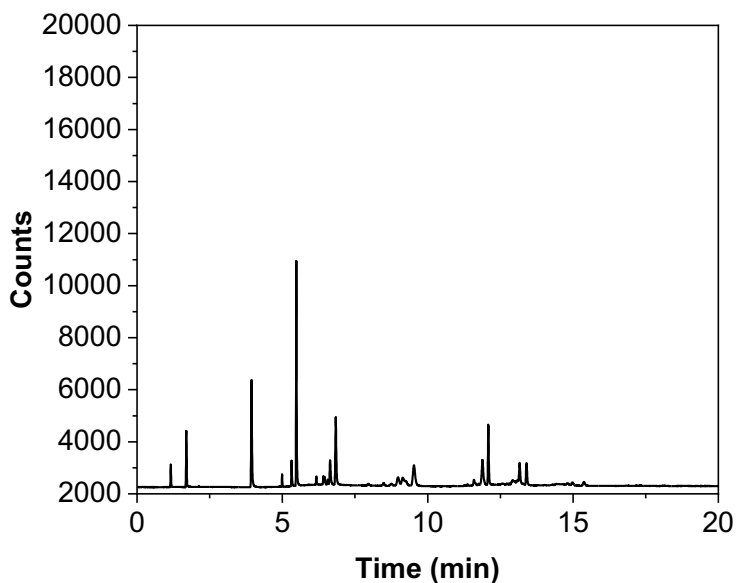
Supplementary Figure 17. GPC analysis of molecular mass and distributions of a commercial PE starting material; $M_n = 2.8$ kDa, $M_w = 5.4$ kDa (Aldrich 332119).



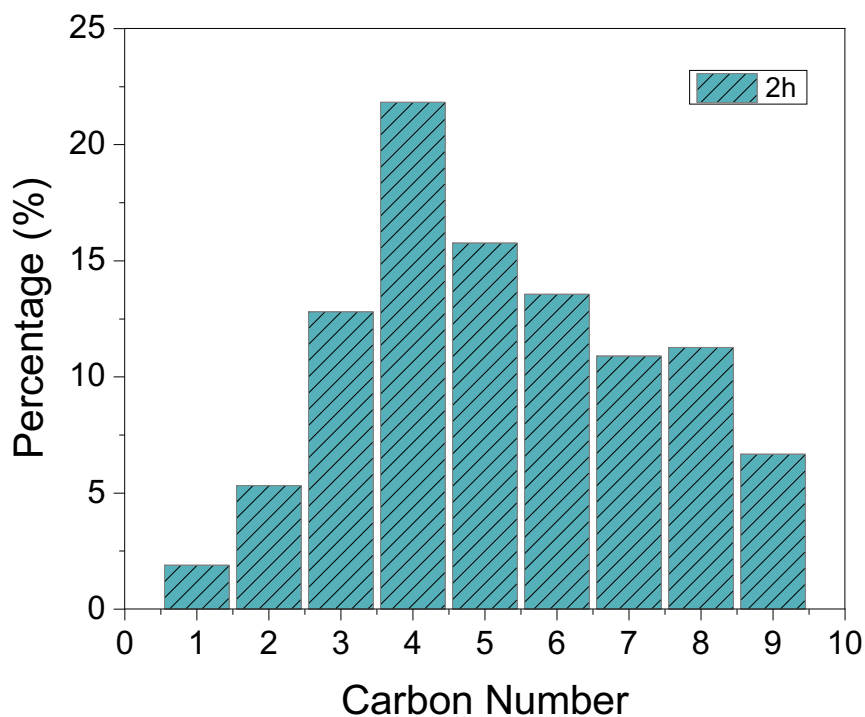
Supplementary Figure 18. GPC analysis of molecular mass and distributions of a post-consumer grocery bag; $M_n = 10.6$ kDa, $M_w = 150.0$ kDa.



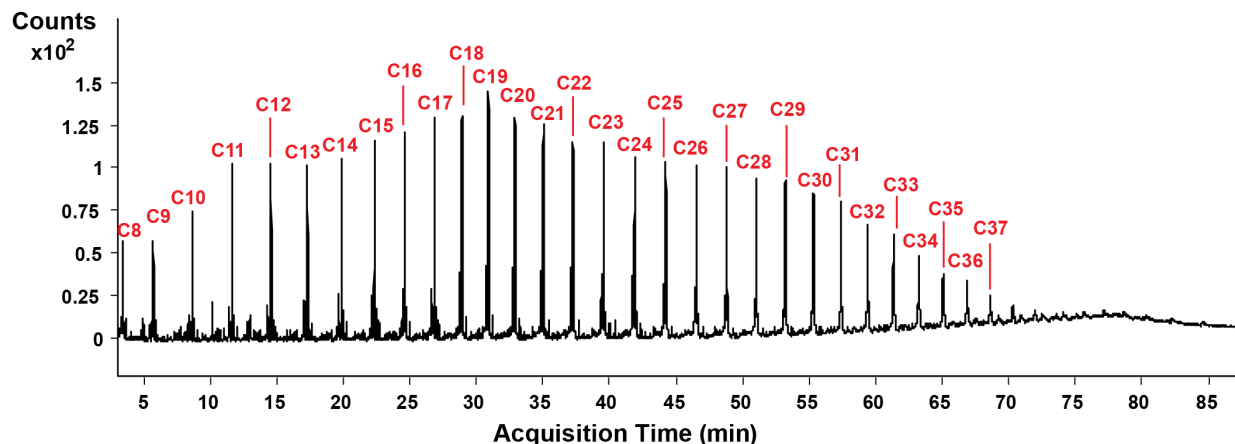
Supplementary Figure 19. TGA-DSC analysis of PE starting material ($M_n = 20$ kDa, $M_w = 90$ kDa) showing its thermal stability above 300 °C.



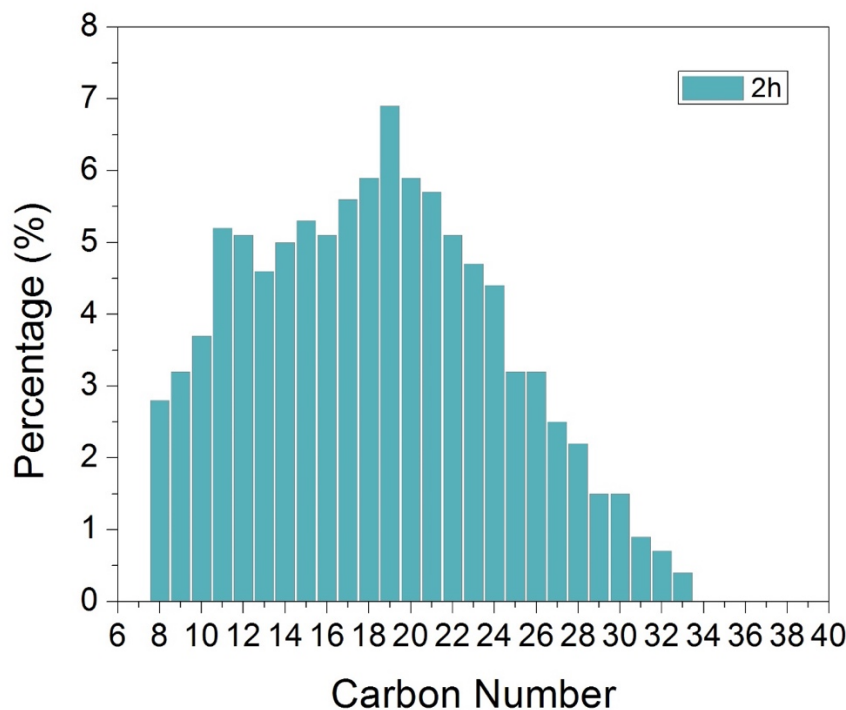
Supplementary Figure 20. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂, yielding 2.2 wt % volatile species with respect to the mass of the starting PE (Supplementary Table 3). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 2 h, 300 °C, under H₂ (0.992 MPa).



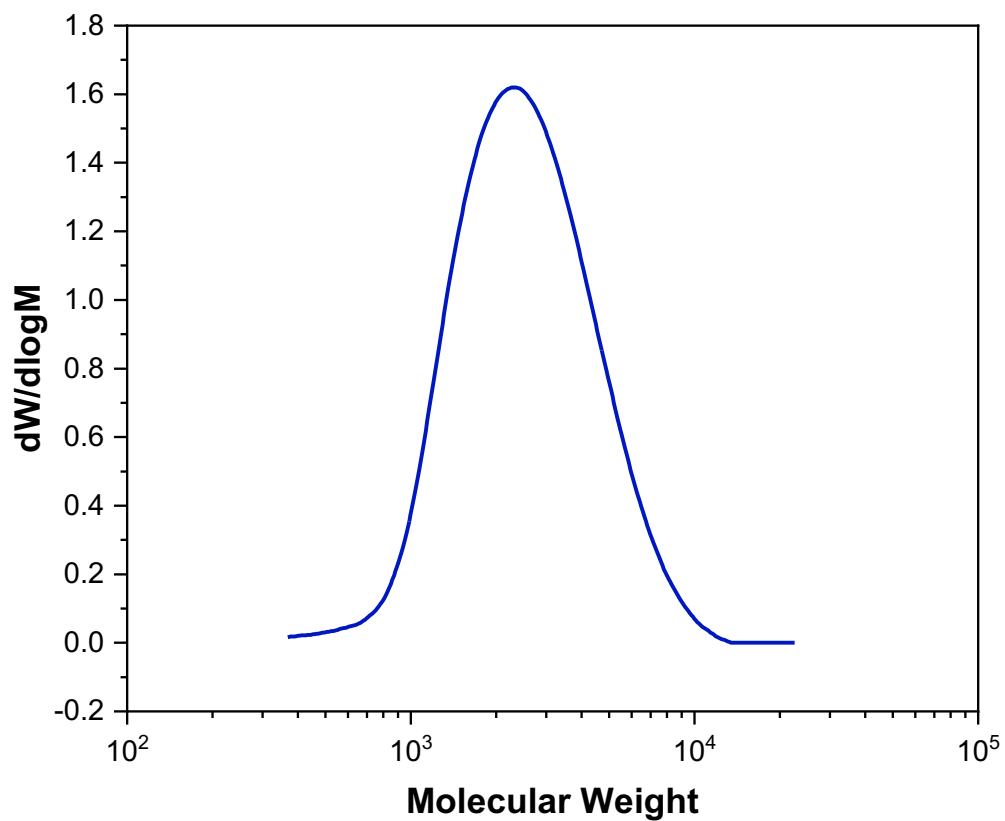
Supplementary Figure 21. Carbon number distribution determined from GC-FID analysis (Supplementary Figure 20) of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 2 h, 300 °C, under H₂ (0.992 MPa).



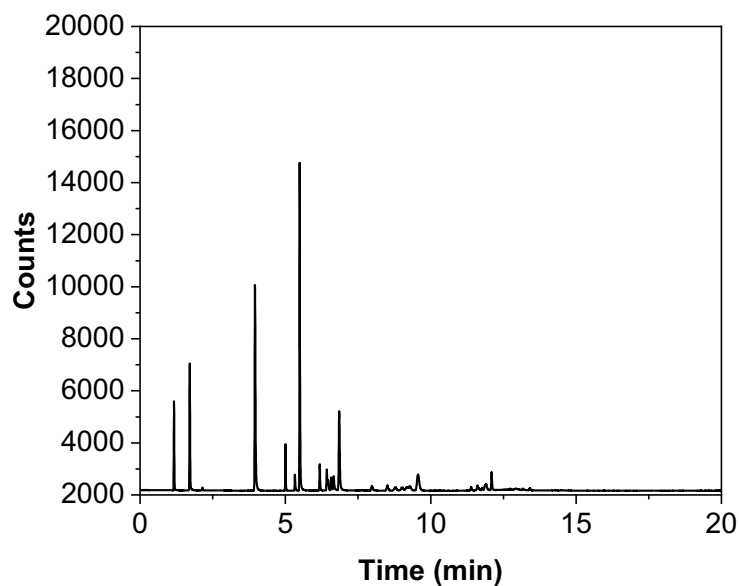
Supplementary Figure 22. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 2 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 15.5% of the mass of the starting PE (Supplementary Table 3).



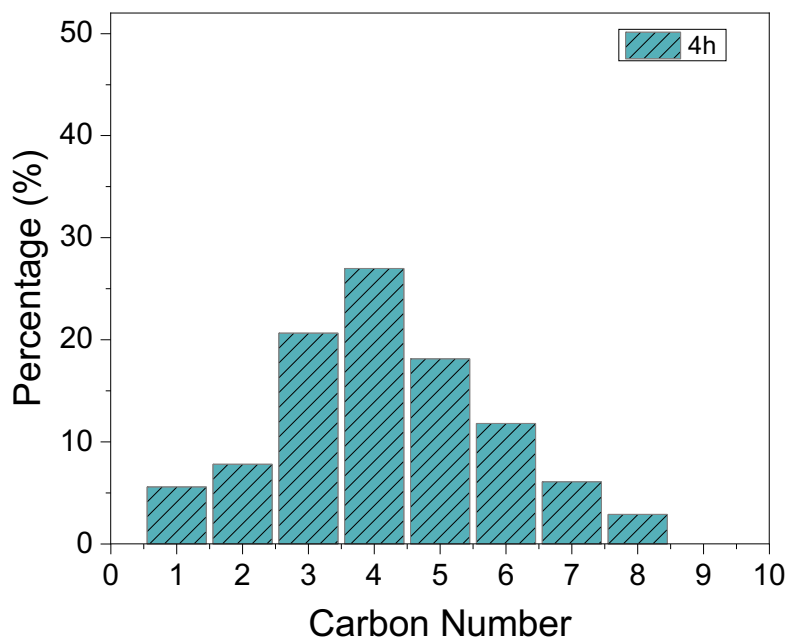
Supplementary Figure 23. Carbon number distribution determined from GC-MS analysis of the oil products (Supplementary Figure 22) generated in the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 2 h, 300 °C, under H₂ (0.992 MPa). These results are duplicated from Figure 4b and 4e)



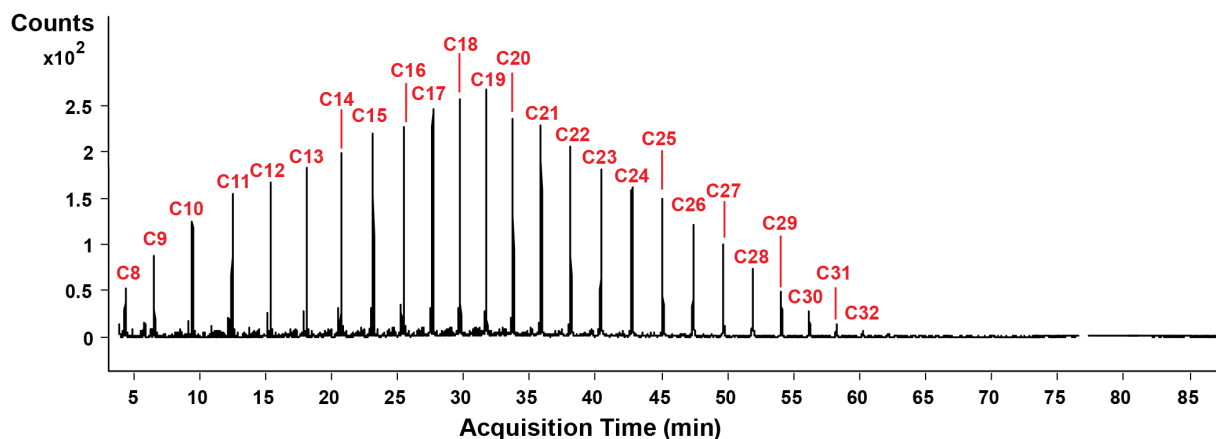
Supplementary Figure 24. GPC trace of the solid remaining after the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ and extraction of oil products with methylene chloride, corresponding to 82.3 wt % solid residue with respect to the mass of the starting PE (Supplementary Table 3). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 2 h, 300 °C, under H₂ (0.992 MPa). $M_n = 3,050$ Da, $M_w = 6,900$ Da, $D = 2.3$ (Supplementary Table 7).



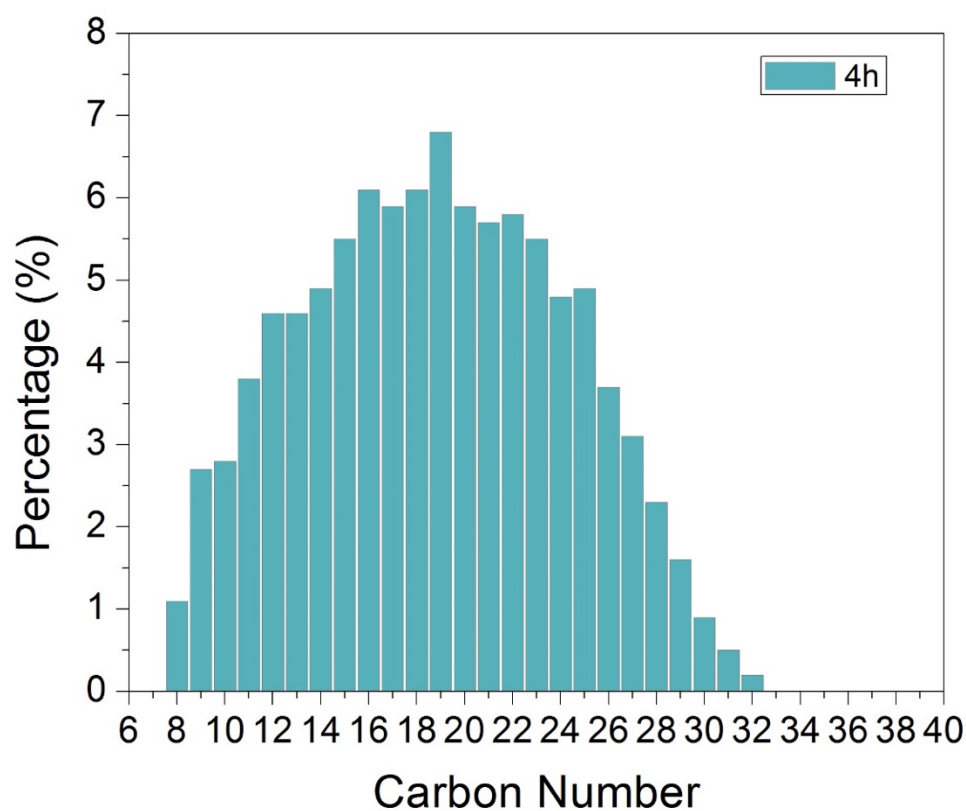
Supplementary Figure 25. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂, yielding 3.0 wt % volatile species with respect to the mass of the starting PE (Supplementary Table 3). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 4 h, 300 °C, under H₂ (0.992 MPa).



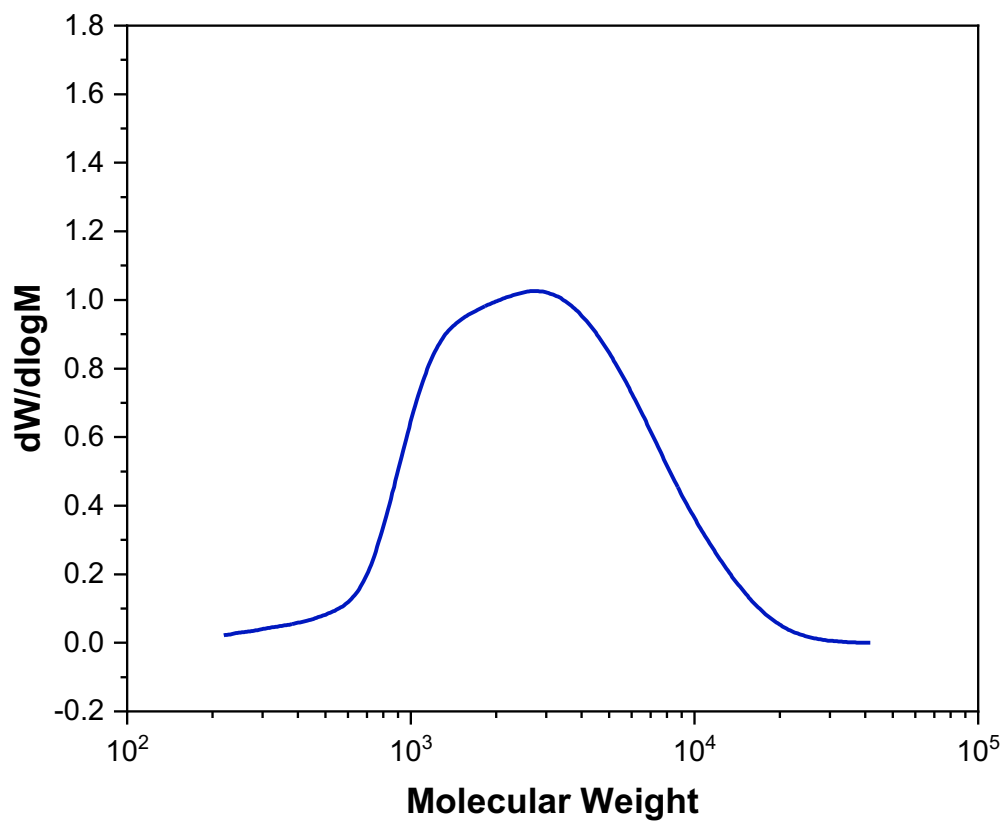
Supplementary Figure 26. Carbon number distribution determined from GC-FID analysis of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ (Supplementary Figure 25). Conditions: 0.0086 ZrO₂ wt / PE wt %, 4 h, 300 °C, under H₂ (0.992 MPa).



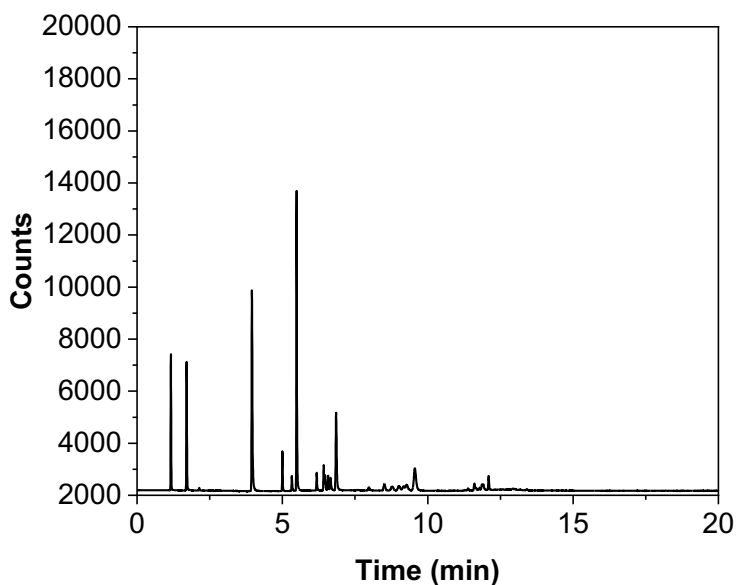
Supplementary Figure 27. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 4 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 27.8% of the mass of the starting PE (Supplementary Table 3).



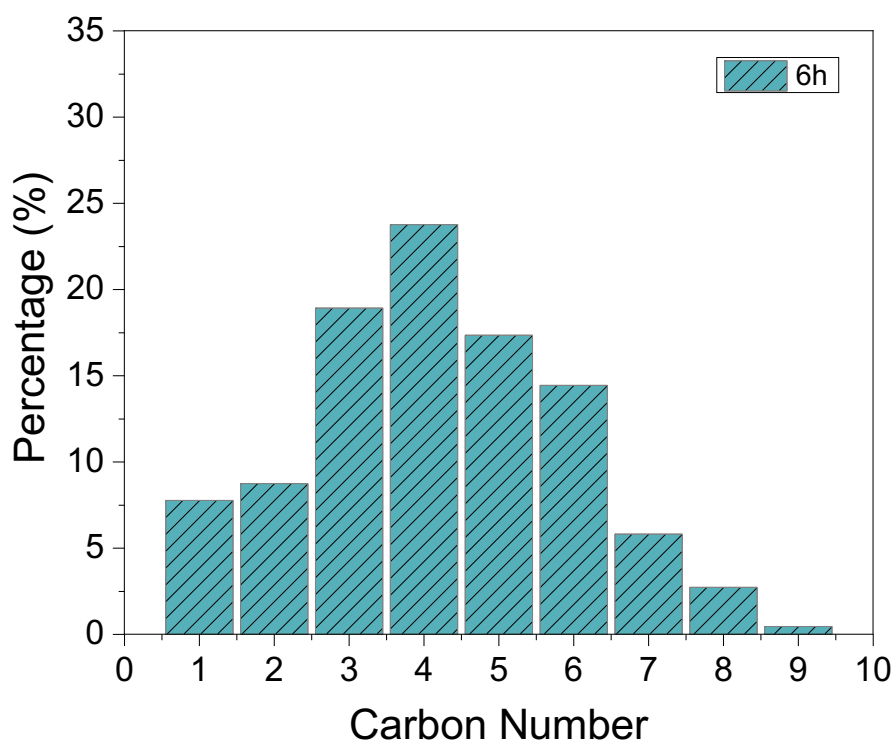
Supplementary Figure 28. Carbon number distribution determined from GC-MS analysis (Supplementary Figure 27) of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 4 h, 300 °C, H₂ (0.992 MPa). These results are duplicated from Figure 4b.



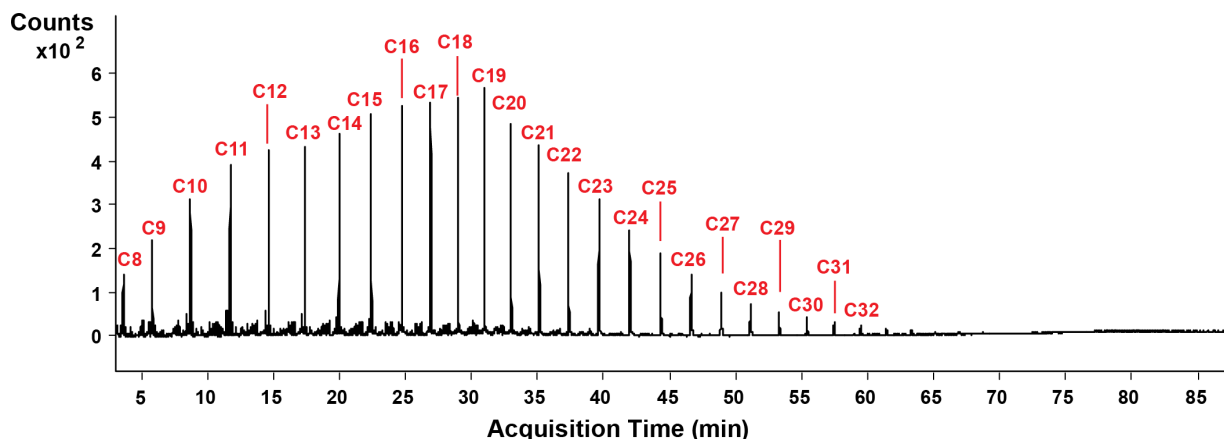
Supplementary Figure 29. GPC trace of the solid left over after the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ after 4 h and extraction of oil products with methylene chloride, corresponding to 69.2 wt % solid residue with respect to the mass of the starting PE (Supplementary Table 3). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 4 h, 300 °C, under H₂ (0.992 MPa). $M_n = 1,990$ Da, $M_w = 3,800$ Da, $D = 1.9$ (Supplementary Table 7).



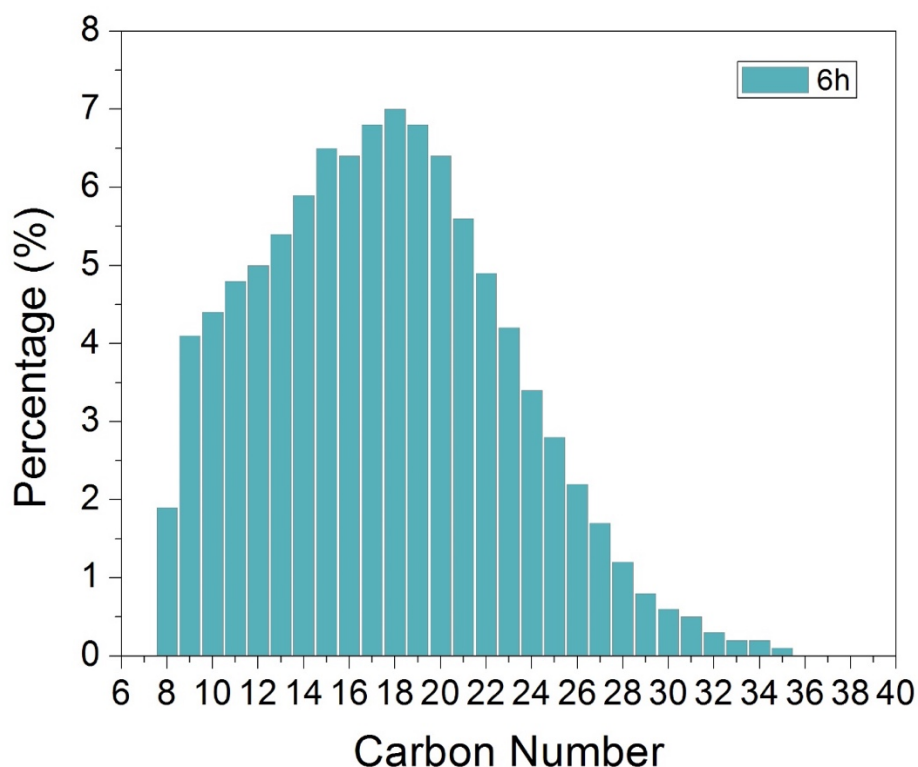
Supplementary Figure 30. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ for 6 h, yielding 2.7 wt % volatile species with respect to the mass of the starting PE (Supplementary Table 3). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



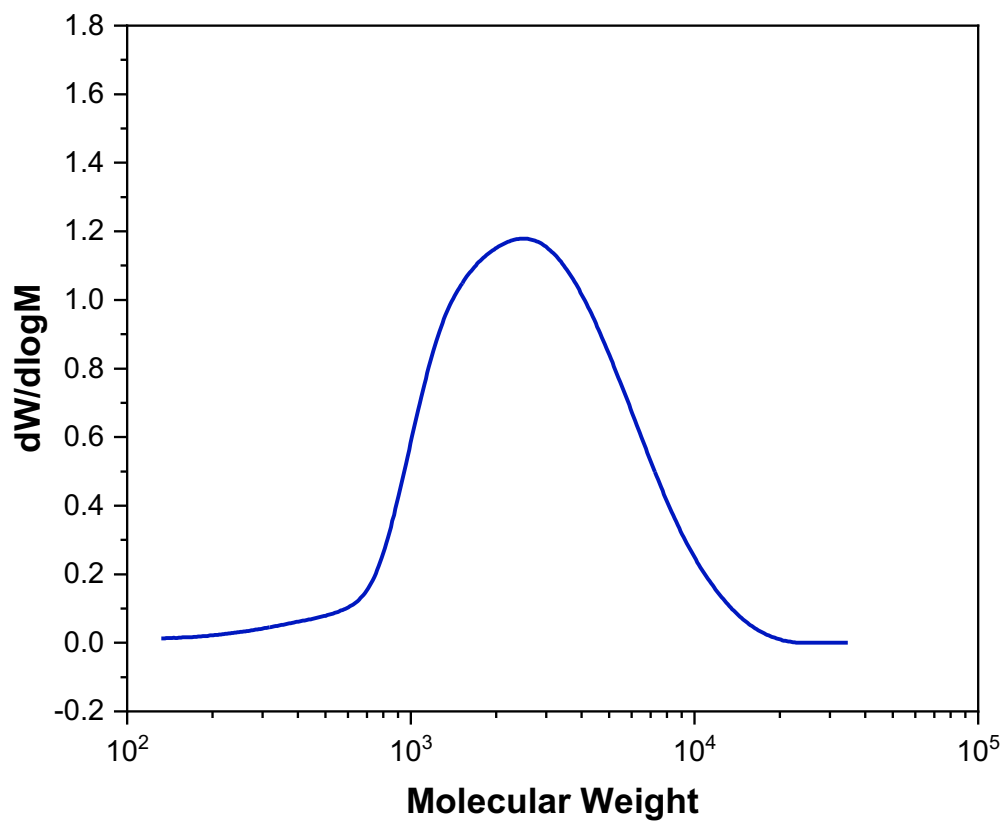
Supplementary Figure 31. Carbon number distribution determined from GC-FID analysis of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ (Supplementary Figure 30). Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



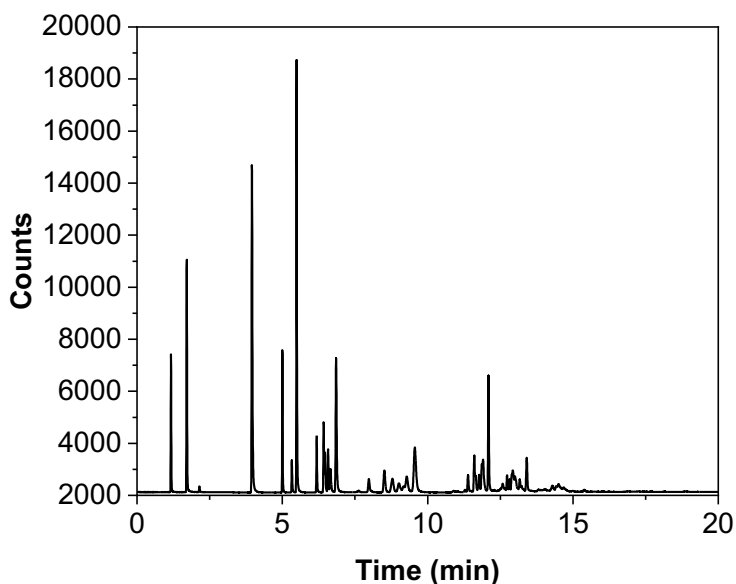
Supplementary Figure 32. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ (Supplementary Table 3). Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 42.3% of the mass of the starting PE.



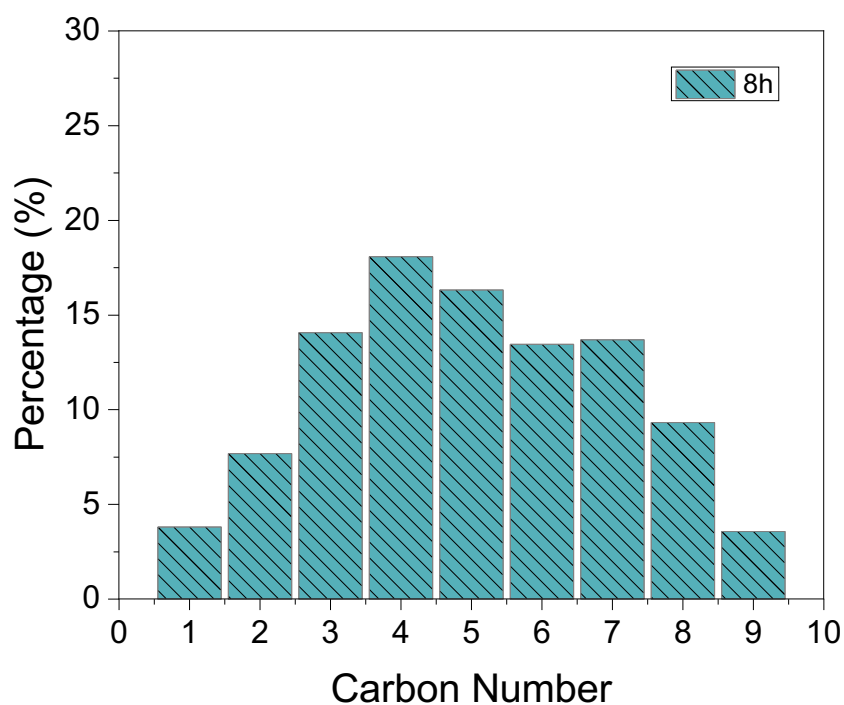
Supplementary Figure 33. Carbon number distribution determined from GC-MS analysis (Supplementary Figure 32) of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa)., These results are duplicated from Figure 4b.



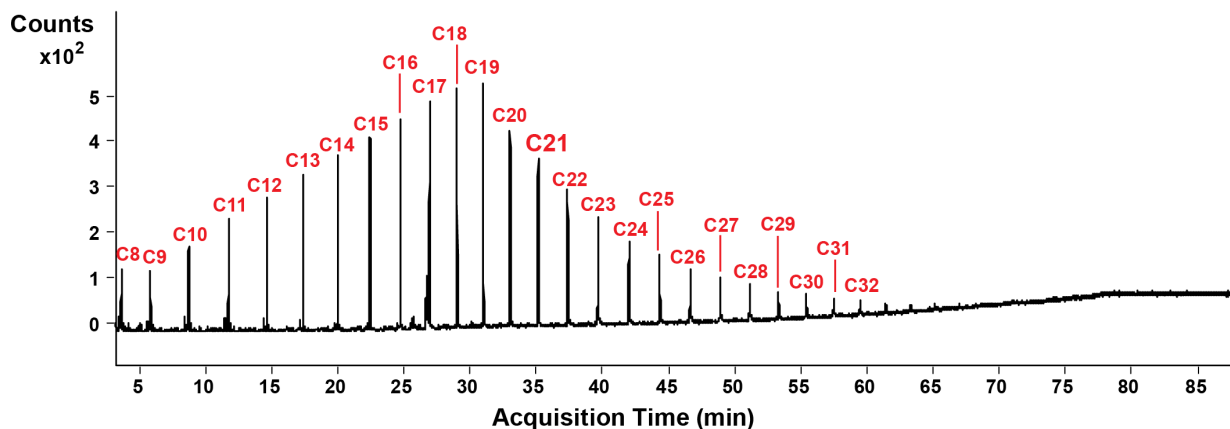
Supplementary Figure 34. GPC trace of the solid remaining after hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ and extraction of oil products with methylene chloride, corresponding to 55.4 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). $M_n = 1,880$ Da, $M_w = 3,300$ Da, $D = 1.8$ (Supplementary Table 7).



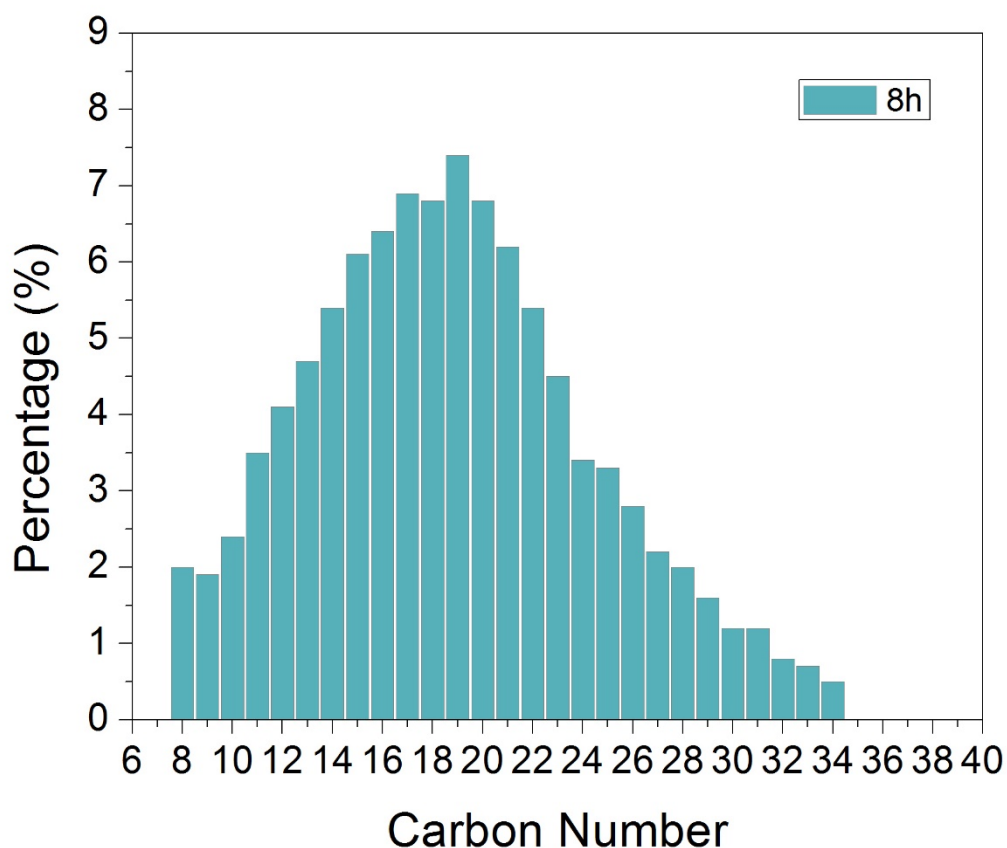
Supplementary Figure 35. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ (Supplementary Table 3), yielding 6.5 wt % volatile species with respect to the mass of the starting PE. Conditions: 0.0086 ZrO₂ wt / PE wt %, 8 h, 300 °C, under H₂ (0.992 MPa).



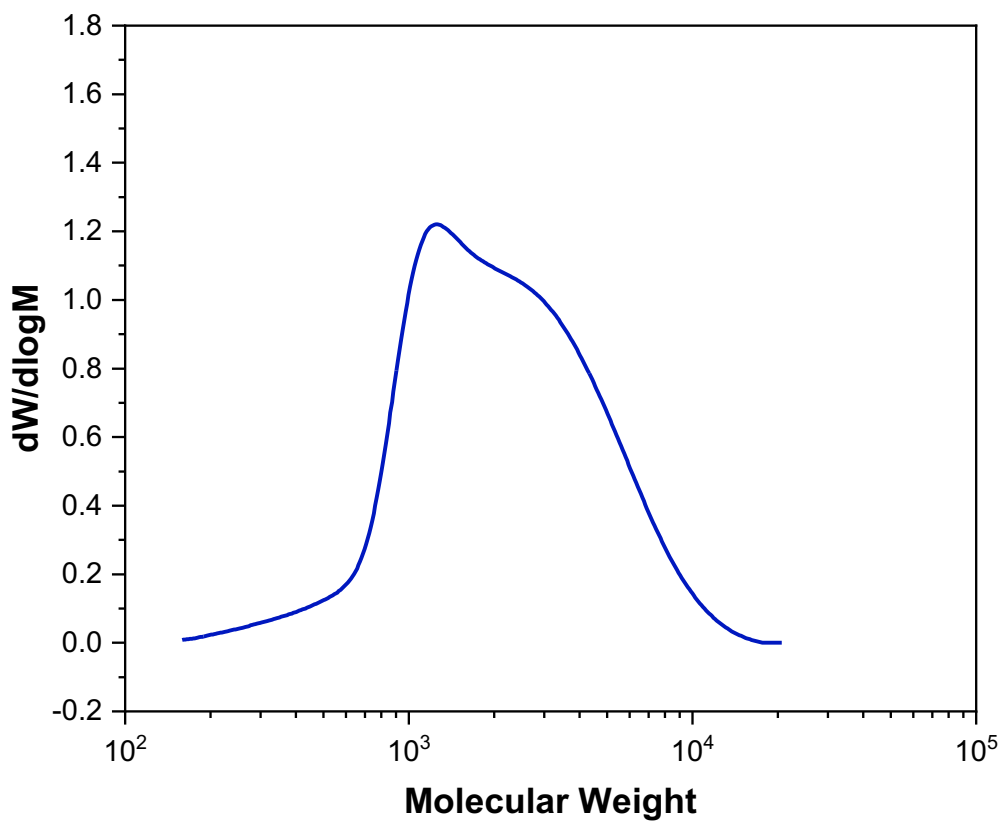
Supplementary Figure 36. Carbon number distribution determined from GC-FID analysis (Supplementary Figure 35) of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 8 h, 300 °C, under H₂ (0.992 MPa).



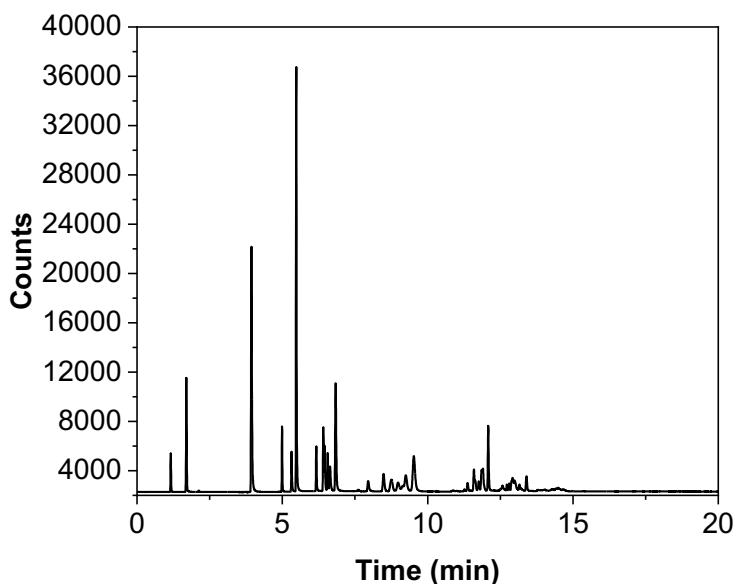
Supplementary Figure 37. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ (Supplementary Table 3). Conditions: 0.0086 ZrO₂ wt / PE wt %, 8 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 55.0% of the mas of the starting PE.



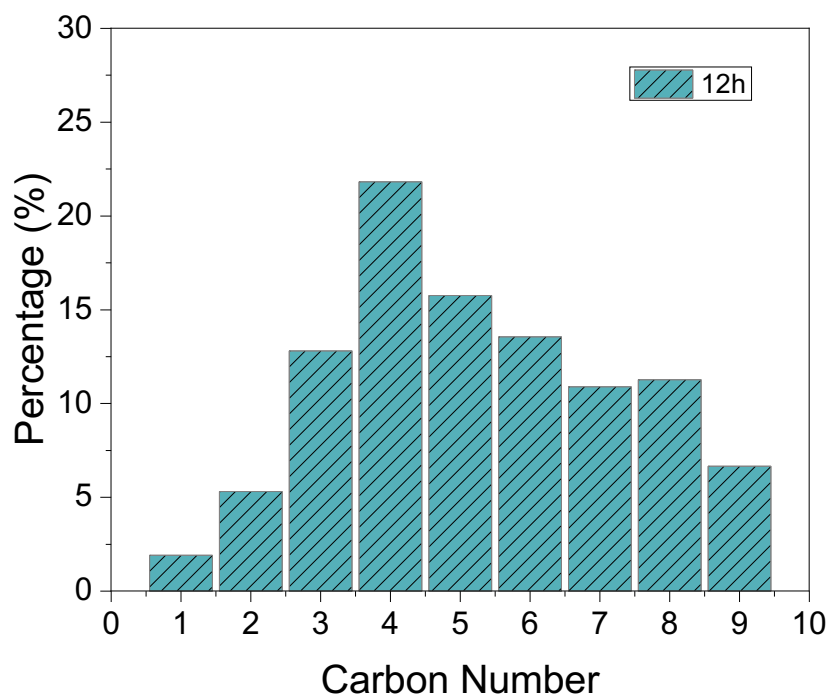
Supplementary Figure 38. Carbon number distribution determined by GC-MS (Supplementary Figure 37) of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ after 8 h. Conditions: 0.0086 ZrO₂ wt / PE wt %, 8 h, 300 °C, under H₂ (0.992 MPa). These results are duplicated from Figure 4b.



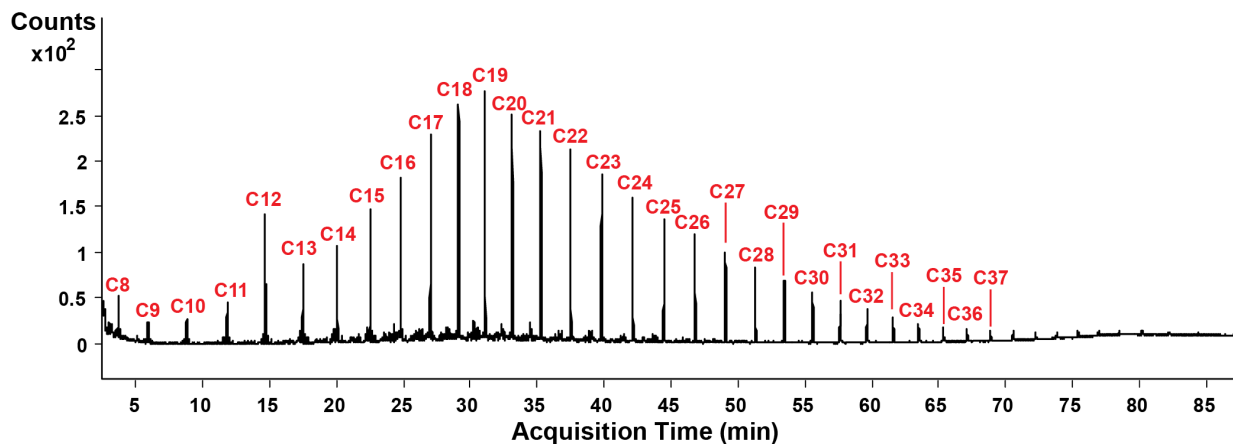
Supplementary Figure 39. GPC trace of the solid remaining after the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ and extraction of oil products with methylene chloride, corresponding to 38.5 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 8 h, 300 °C, under H₂ (0.992 MPa). $M_n = 1,600$ Da, $M_w = 2,700$ Da, $\mathcal{D} = 1.7$ (Supplementary Table 7).



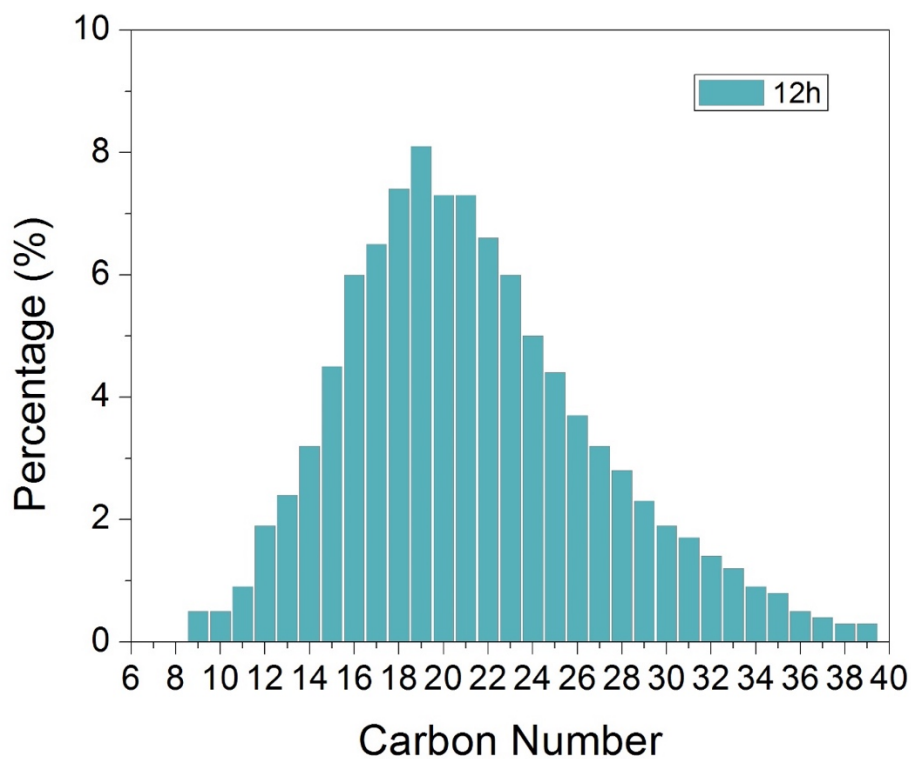
Supplementary Figure 40. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂, yielding 7.7 wt % volatile species with respect to the mass of the starting PE (Supplementary Table 3). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 12 h, 300 °C, under H₂ (0.992 MPa).



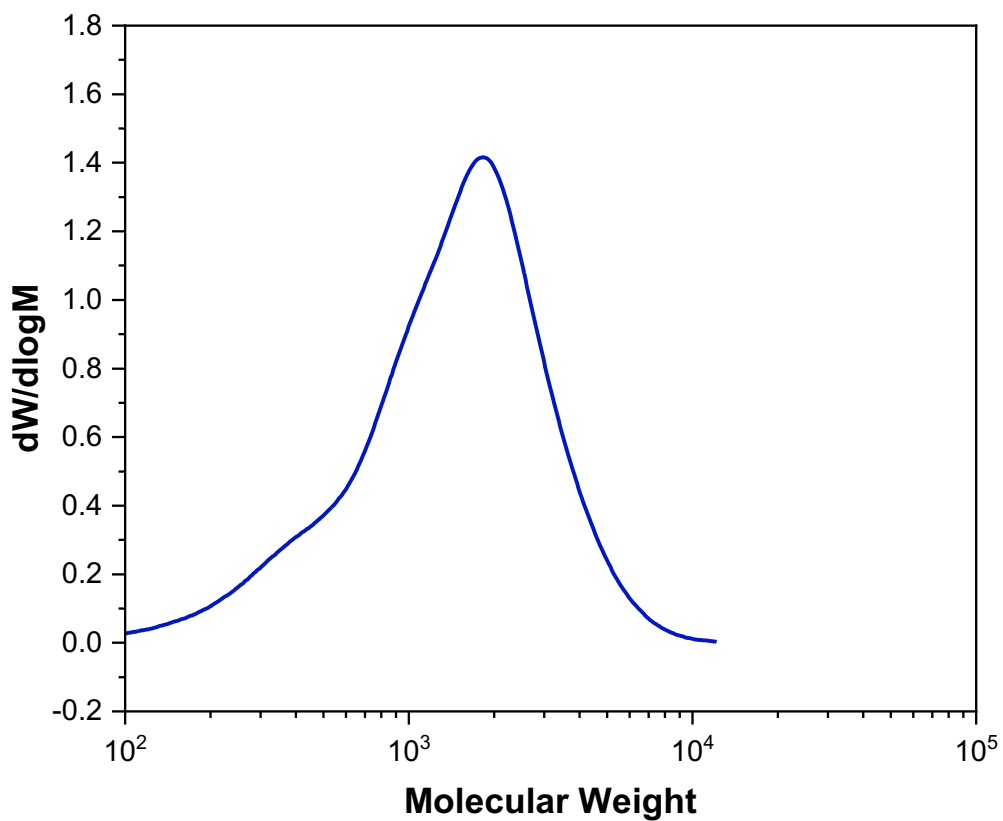
Supplementary Figure 41. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 40) of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 12 h, 300 °C, under H₂ (0.992 MPa).



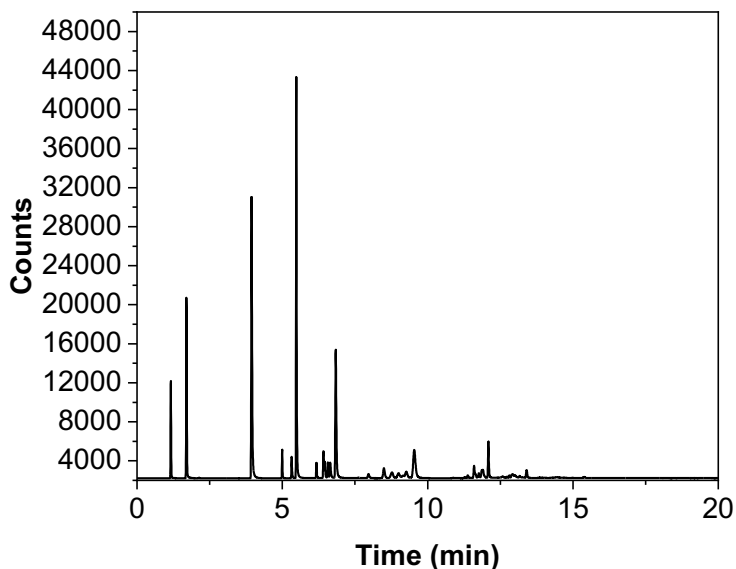
Supplementary Figure 42. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt % / PE wt %, 12 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 64.9% of the mass of the starting PE (Supplementary Table 3).



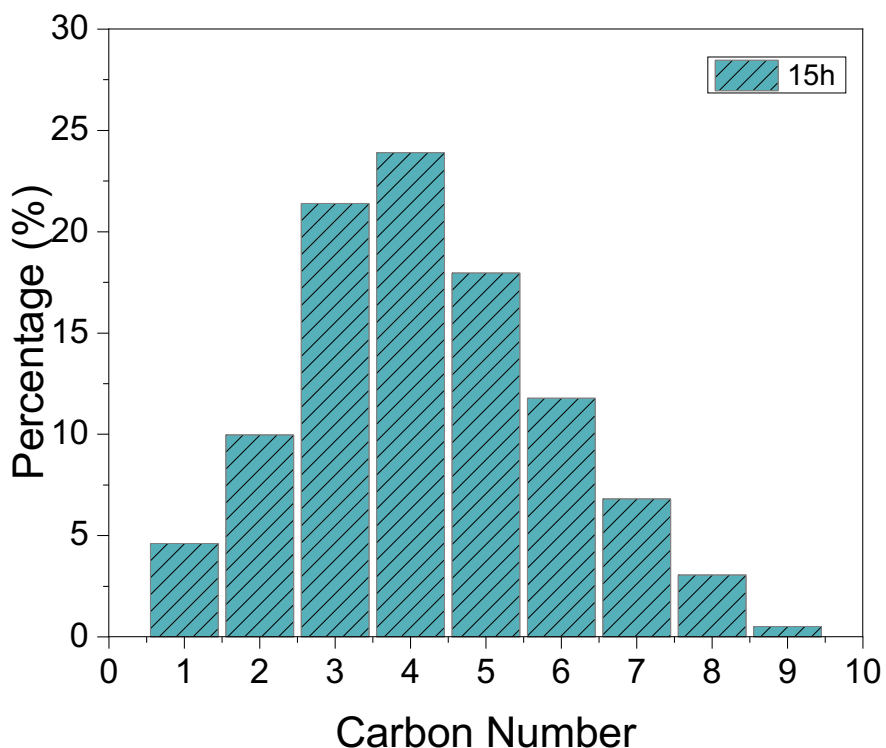
Supplementary Figure 43. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 42) of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt % / PE wt %, 12 h, 300 °C, under H₂ (0.992 MPa). These results are duplicated from Figure 4b.



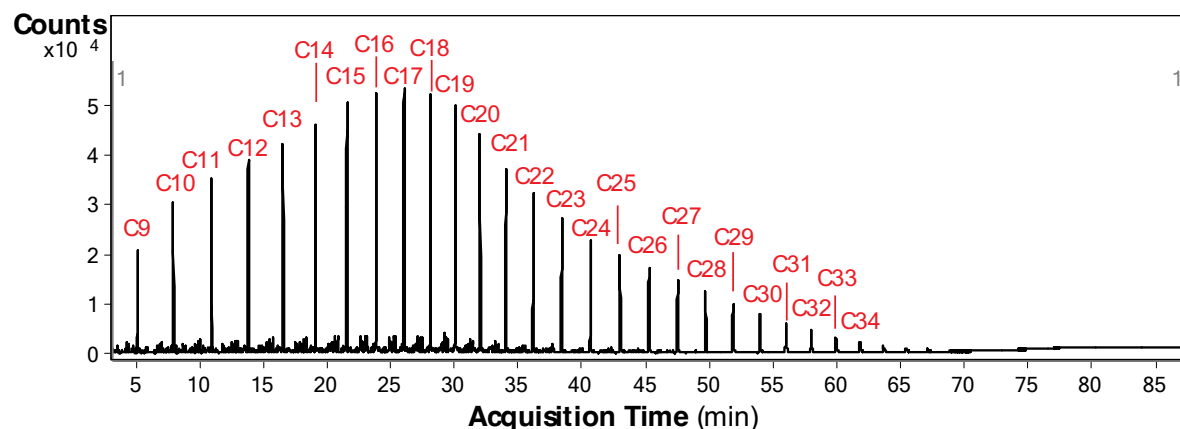
Supplementary Figure 44. GPC trace of the solid remaining after the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ and extraction of soluble oils using methylene chloride, corresponding to 27.4 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 12 h, 300 °C, under H₂ (0.992 MPa). $M_n = 930$ Da, $M_w = 1,800$ Da, $\bar{D} = 1.9$ (Supplementary Table 7).



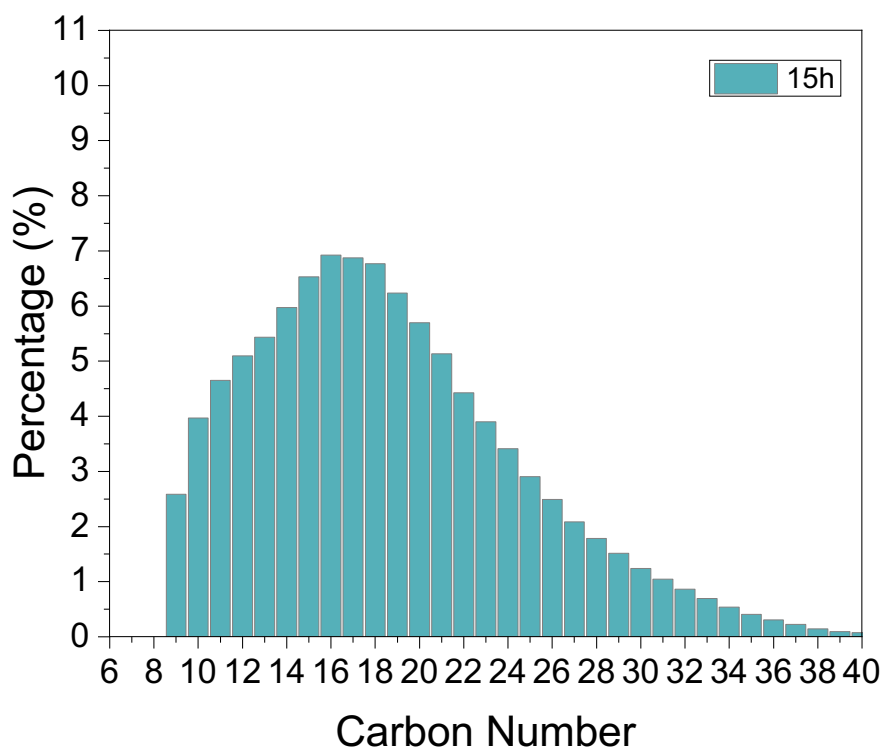
Supplementary Figure 45. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂, yielding 9.8 wt % volatile species with respect to the mass of the starting PE (Supplementary Table 3). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 15 h, 300 °C, under H₂ (0.992 MPa).



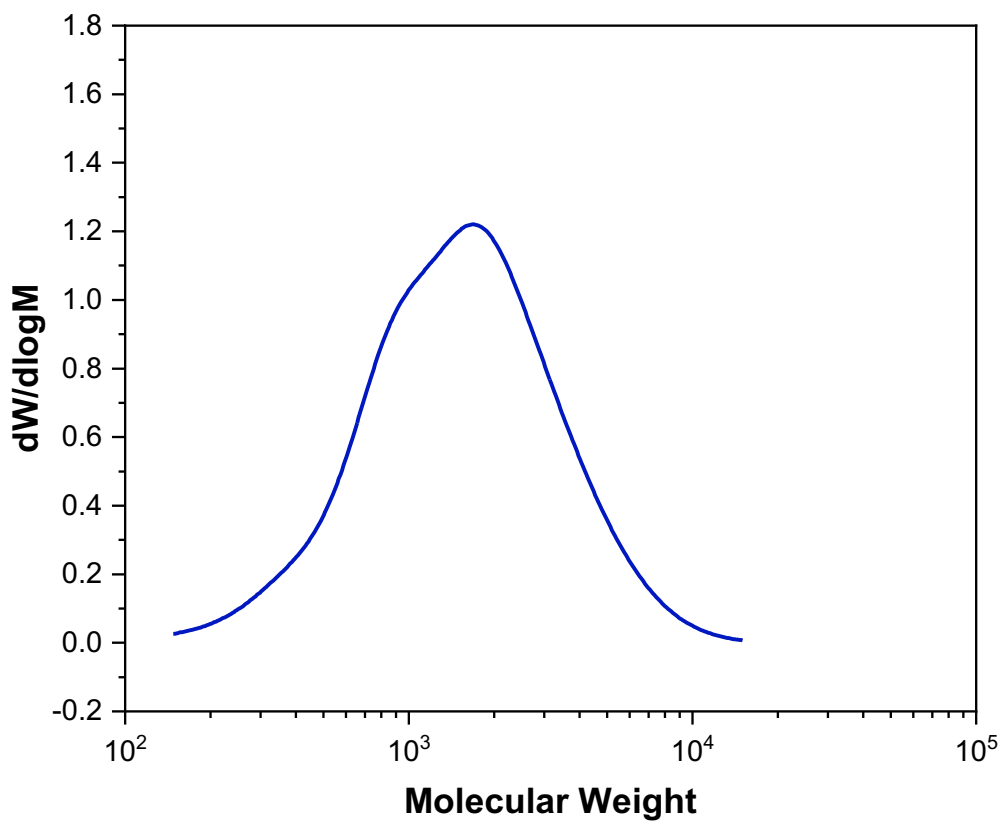
Supplementary Figure 46. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 45) of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 15 h, 300 °C, under H₂ (0.992 MPa).



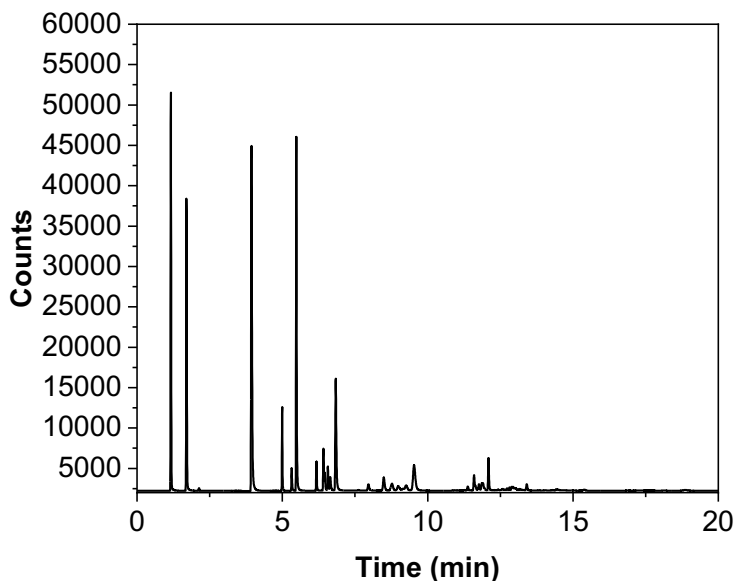
Supplementary Figure 47. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ over 15 h (Supplementary Table 3). Conditions: 0.0086 ZrO₂ wt / PE wt %, 15 h, 300 °C, H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 79.8% of the mass of the starting PE.



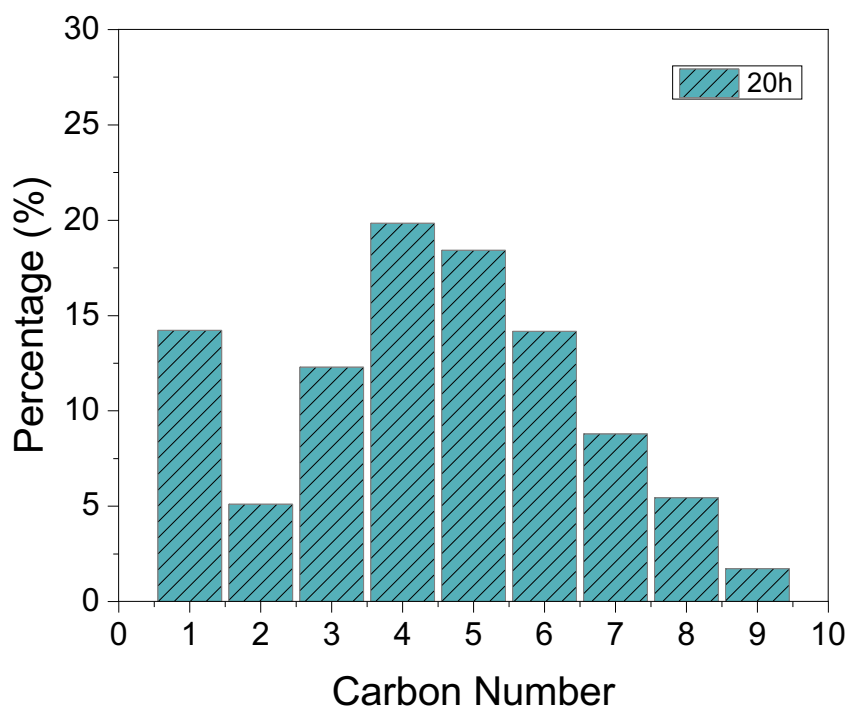
Supplementary Figure 48. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 47) of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 15 h, 300 °C, under H₂ (0.992 MPa).



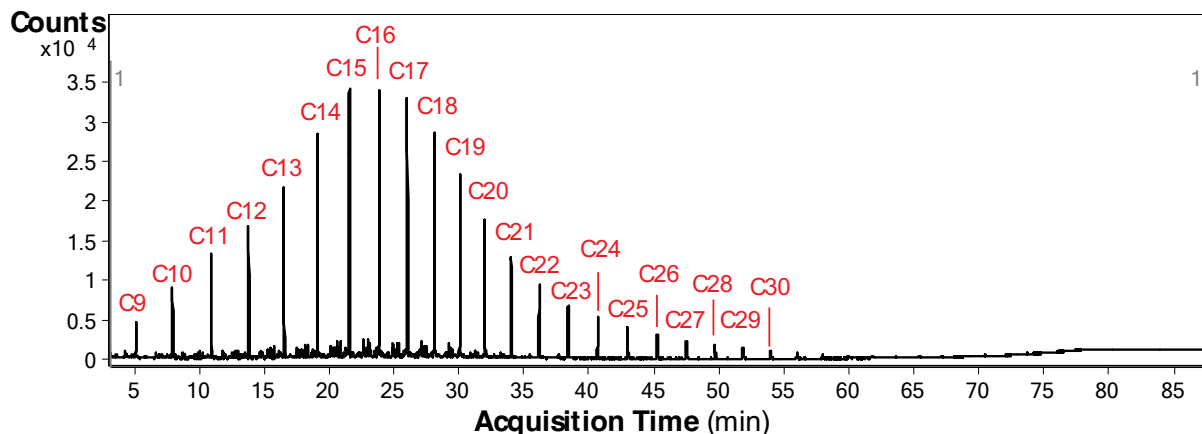
Supplementary Figure 49. GPC trace of the solid remaining after the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ and extraction of the soluble oil with methylene chloride, yielding 82.3 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 15 h, 300 °C, under H₂ (0.992 MPa). $M_n = 1,100$ Da, $M_w = 1,990$ Da, $\bar{D} = 1.8$ (Supplementary Table 7).



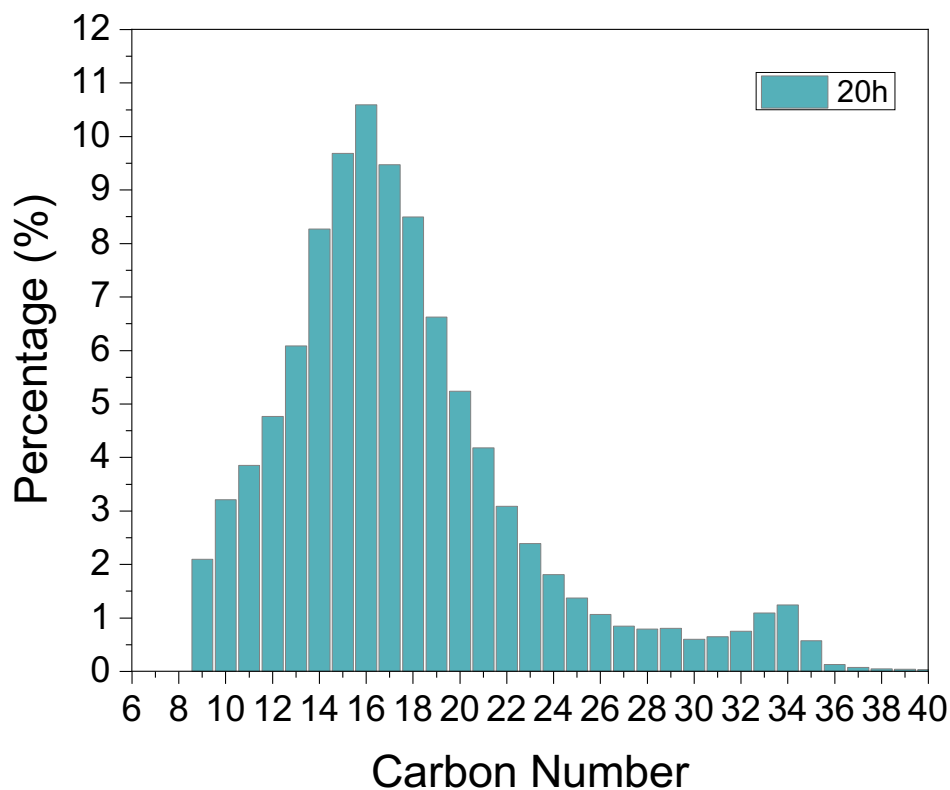
Supplementary Figure 50. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂, yielding 14.2 wt % volatile species with respect to the mass of the starting PE (Supplementary Table 3). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 20 h, 300 °C, under H₂ (0.992 MPa).



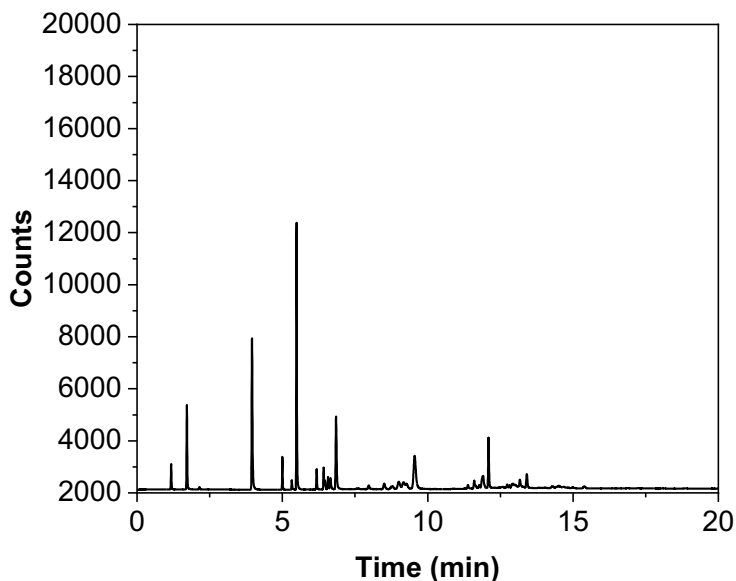
Supplementary Figure 51. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 50) of the sampled headspace from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 20 h, 300 °C, under H₂ (0.992 MPa).



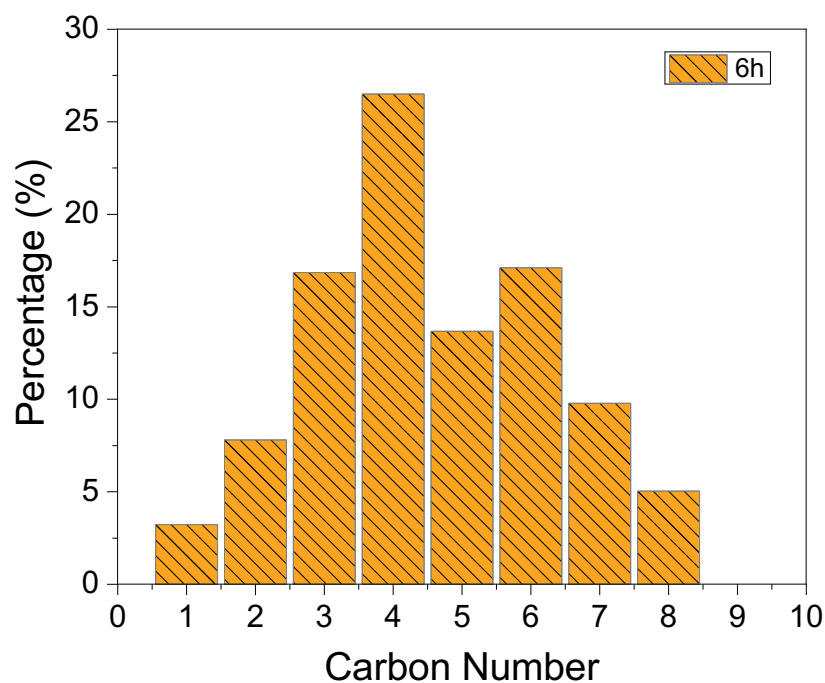
Supplementary Figure 52. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂ (Supplementary Table 3). Conditions: 0.0086 ZrO₂ wt / PE wt %, 20 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 85.8% of the mass of the starting PE.



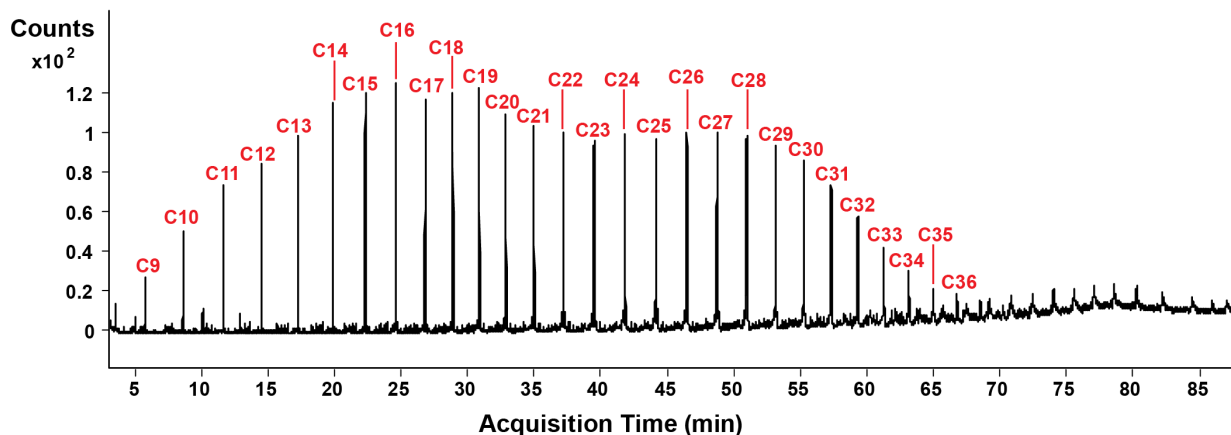
Supplementary Figure 53. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 52) of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 20 h, 300 °C, under H₂ (0.992 MPa). These results are duplicated from Figure 4b.



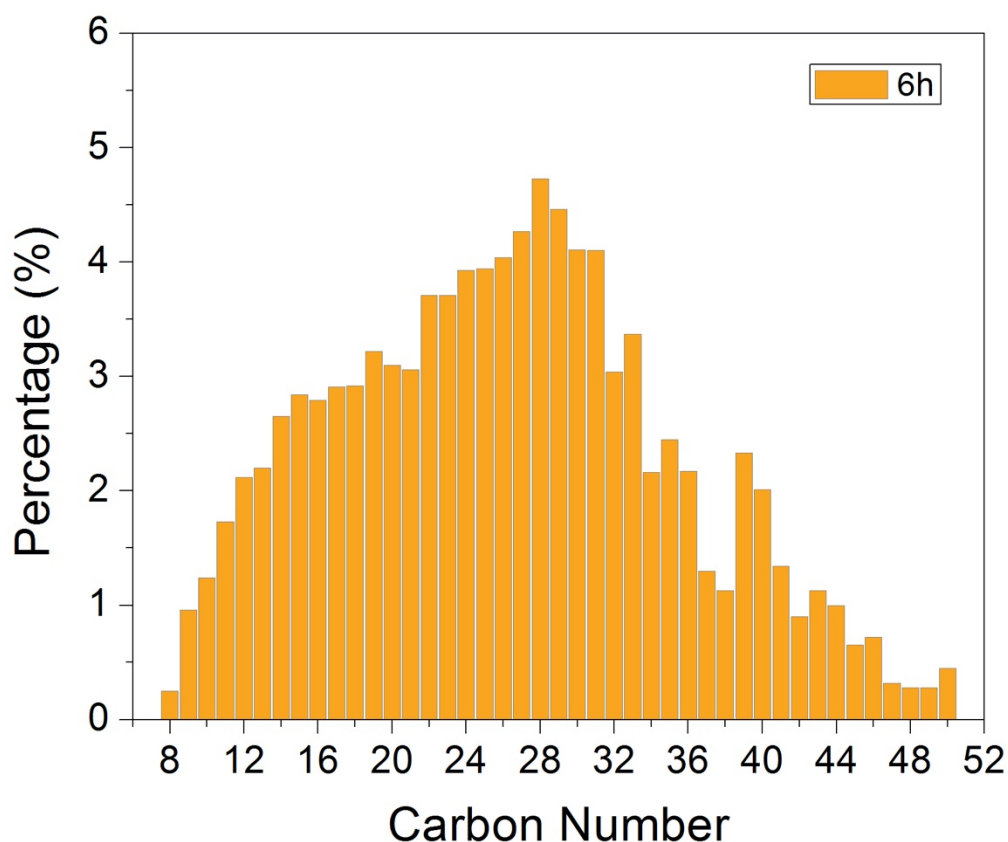
Supplementary Figure 54. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by imp-ZrO₂/mSiO₂, yielding 2.6% volatile species with respect to the mass of the starting PE (Supplementary Table 4). Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



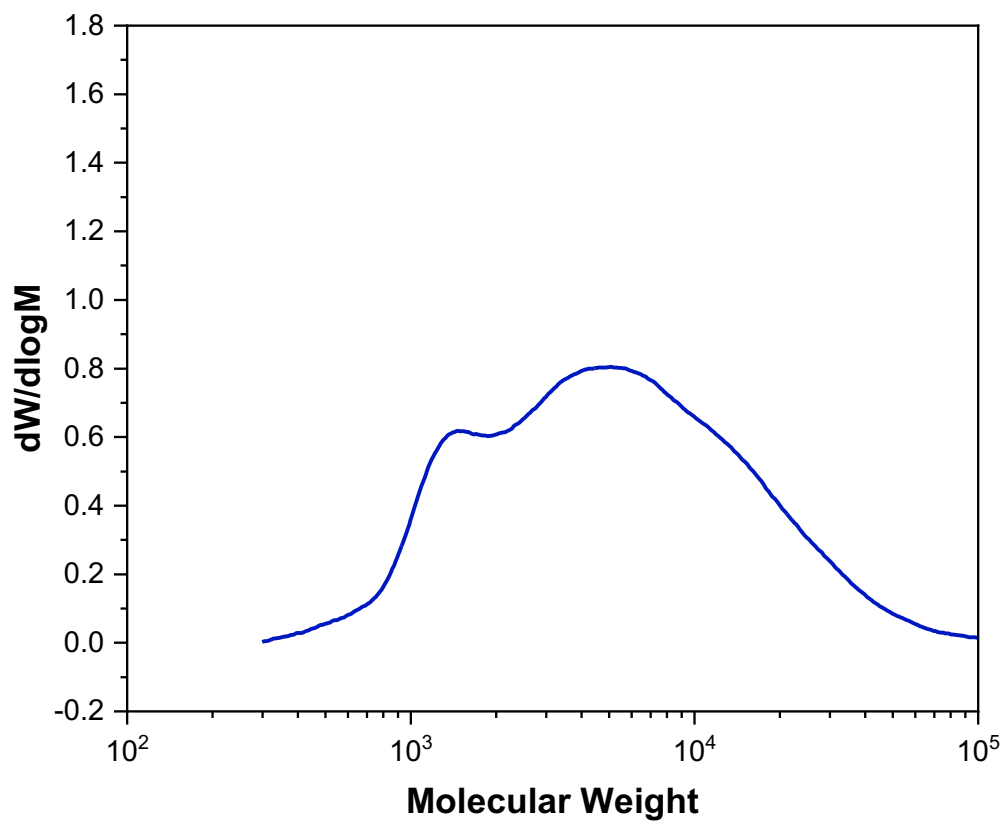
Supplementary Figure 55. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 54) of the sampled headspace from the hydrogenolysis of PE catalyzed by imp-ZrO₂/mSiO₂ (Supplementary Table 4). Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



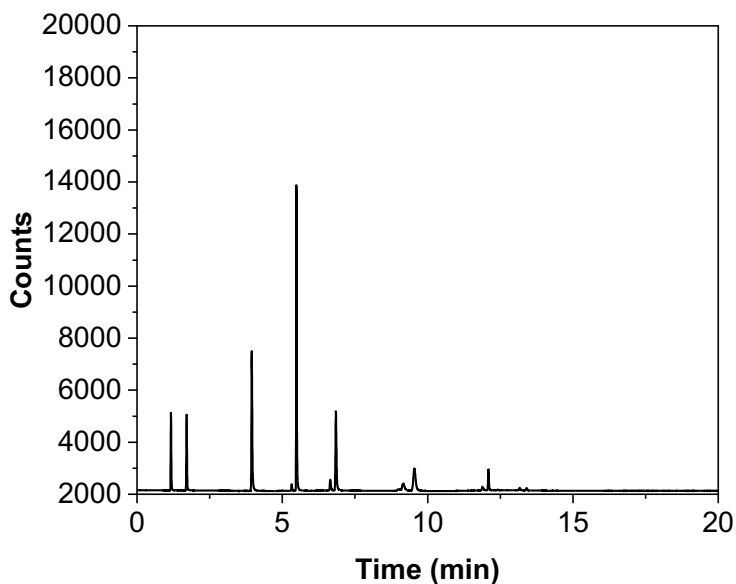
Supplementary Figure 56. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by imp-ZrO₂/SiO₂ (Supplementary Table 4). Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 20.1% of the mass of the starting PE.



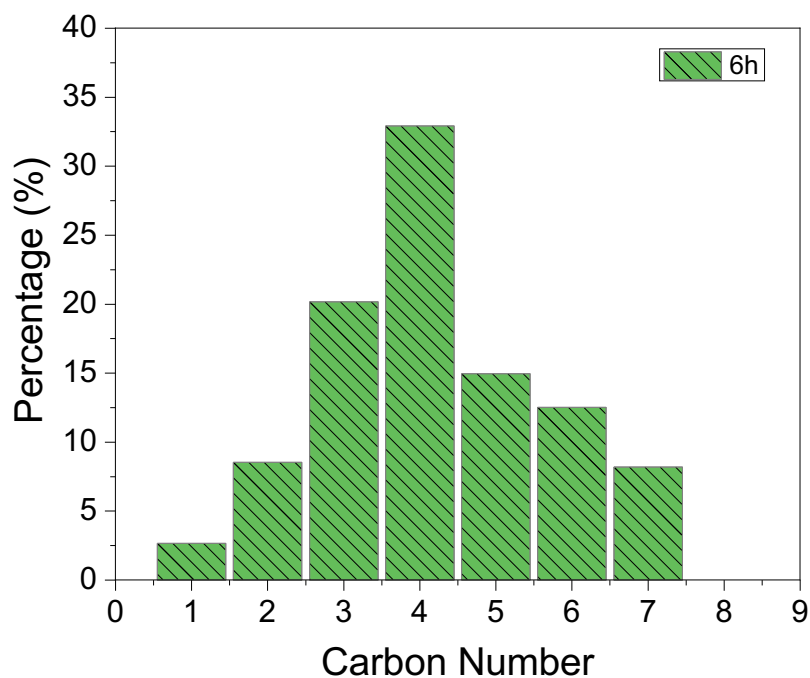
Supplementary Figure 57. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 56) of the oil products from the hydrogenolysis of PE catalyzed by imp-ZrO₂/mSiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). These results are duplicated from Figure 4e.



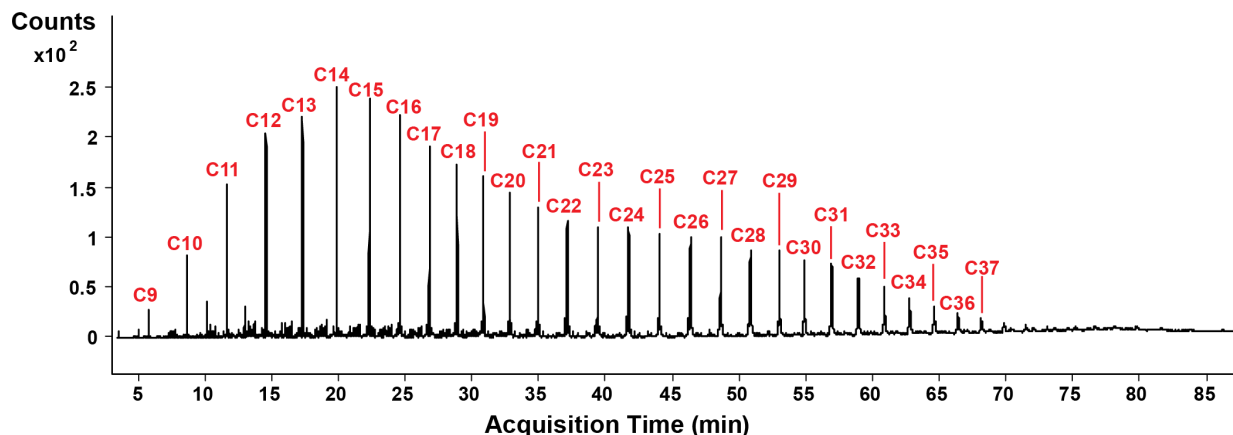
Supplementary Figure 58. GPC trace of the solid remaining after hydrogenolysis of PE catalyzed by imp-ZrO₂/mSiO₂ and extraction of oils using methylene chloride, yielding 77.4 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). $M_n = 3,000$ Da, $M_w = 8,700$ Da, $\bar{D} = 2.9$ (Supplementary Table 7).



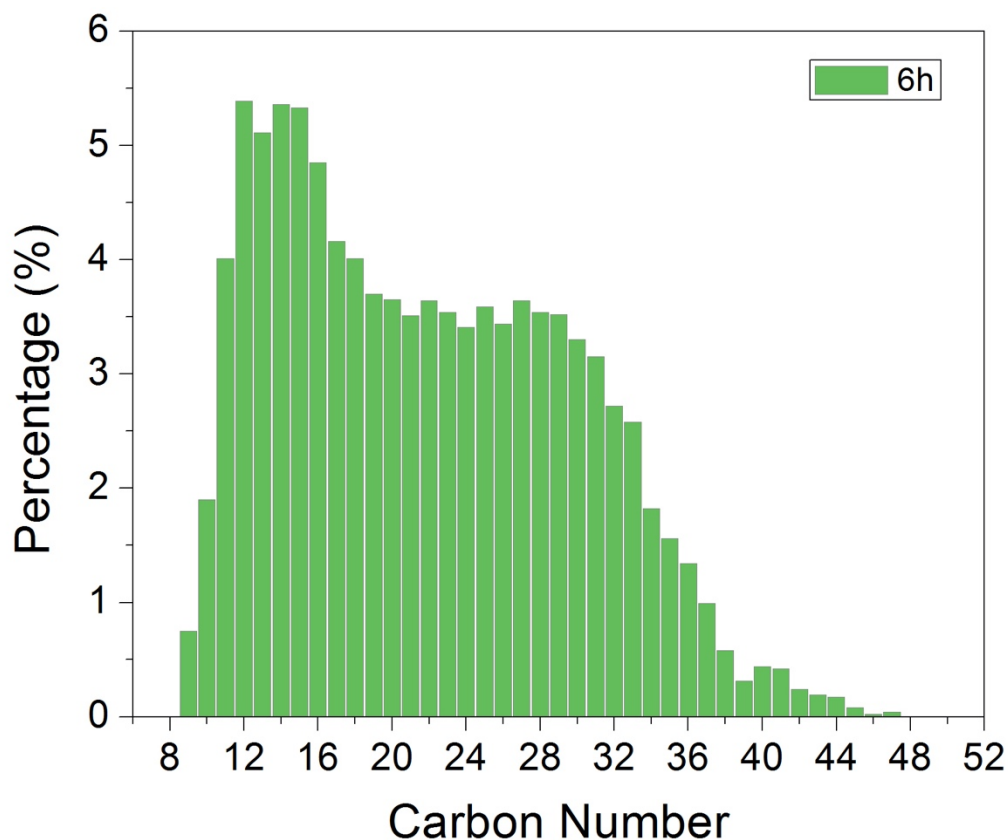
Supplementary Figure 59. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-6/mSiO}_2$, yielding 0.7% volatile species with respect to the mass of the starting PE (Supplementary Table 4). Conditions: 0.0119 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa).



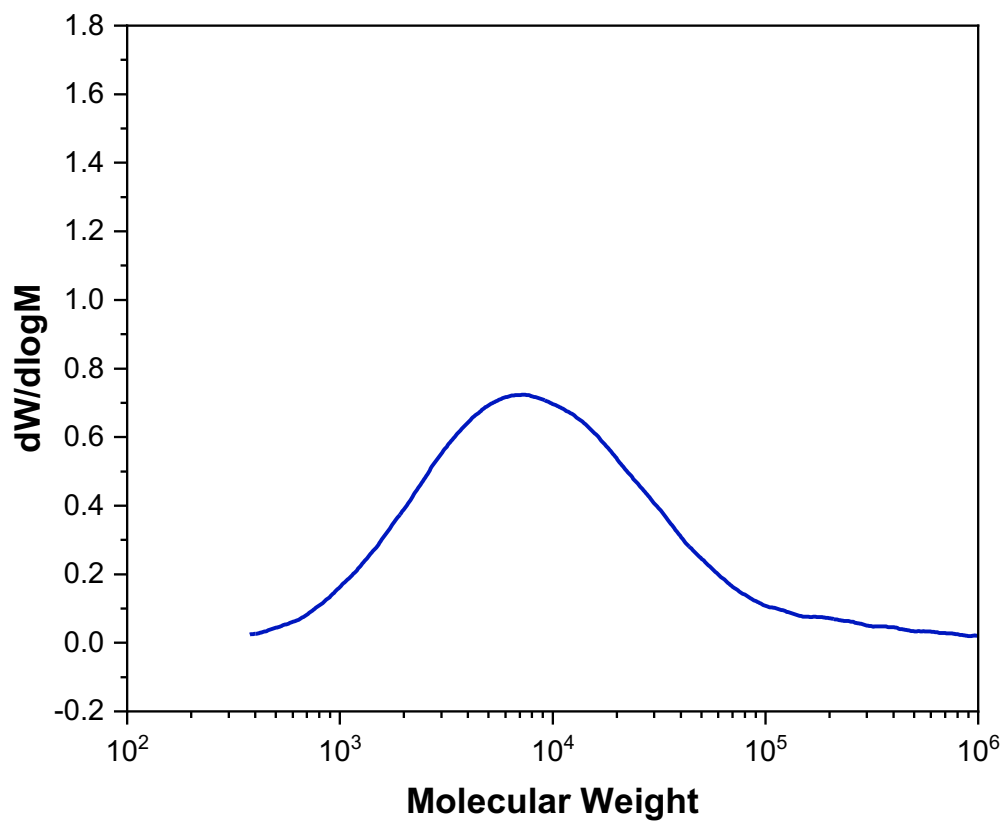
Supplementary Figure 60. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 59) of the sampled headspace from the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-6/mSiO}_2$. Conditions: 0.0119 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa).



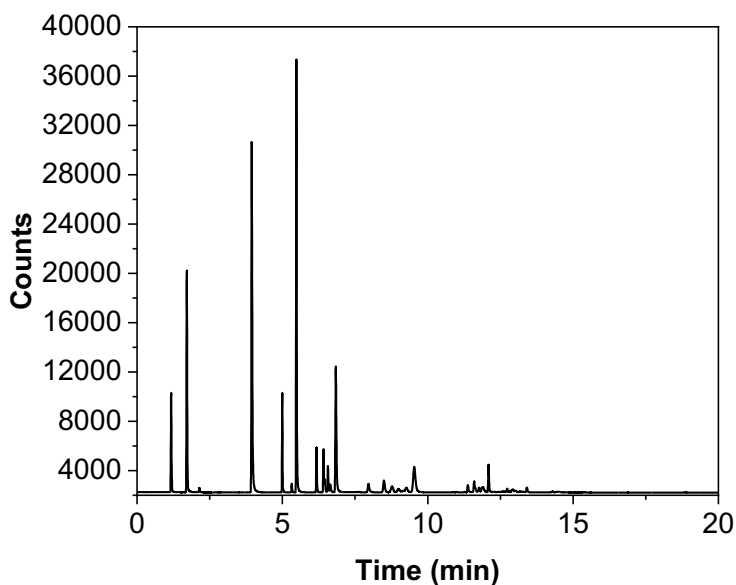
Supplementary Figure 61. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-6/mSiO}_2$. Conditions: 0.0119 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 12.6% of the mass of the starting PE (Supplementary Table 4).



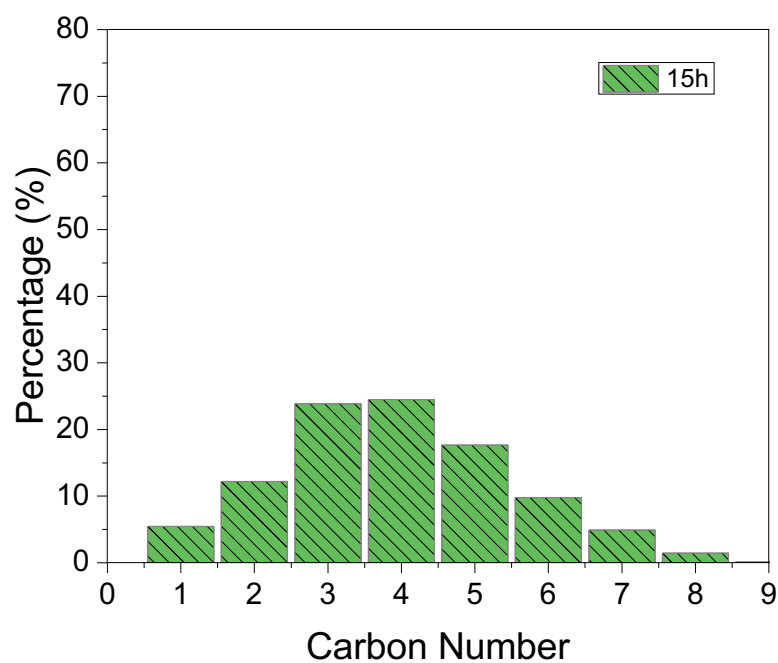
Supplementary Figure 62. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 61) of the oil products from the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-6/mSiO}_2$. Conditions: 0.0119 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa).



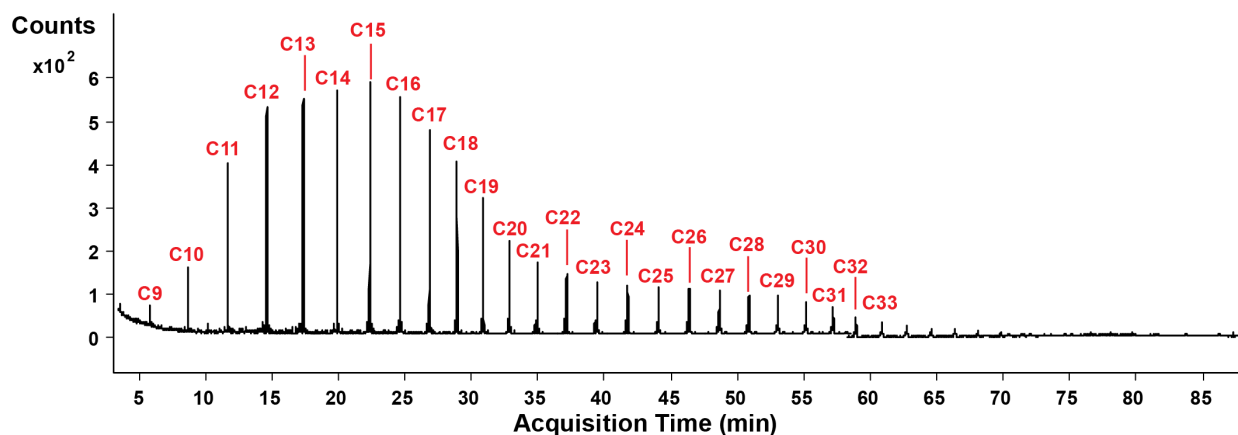
Supplementary Figure 63. GPC trace of the solid left over from the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-6/mSiO}_2$, yielding 86.7 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.0119 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa). $M_n = 4,500$ Da, $M_w = 29,600$ Da, $\bar{D} = 6.6$ (Supplementary Table 7).



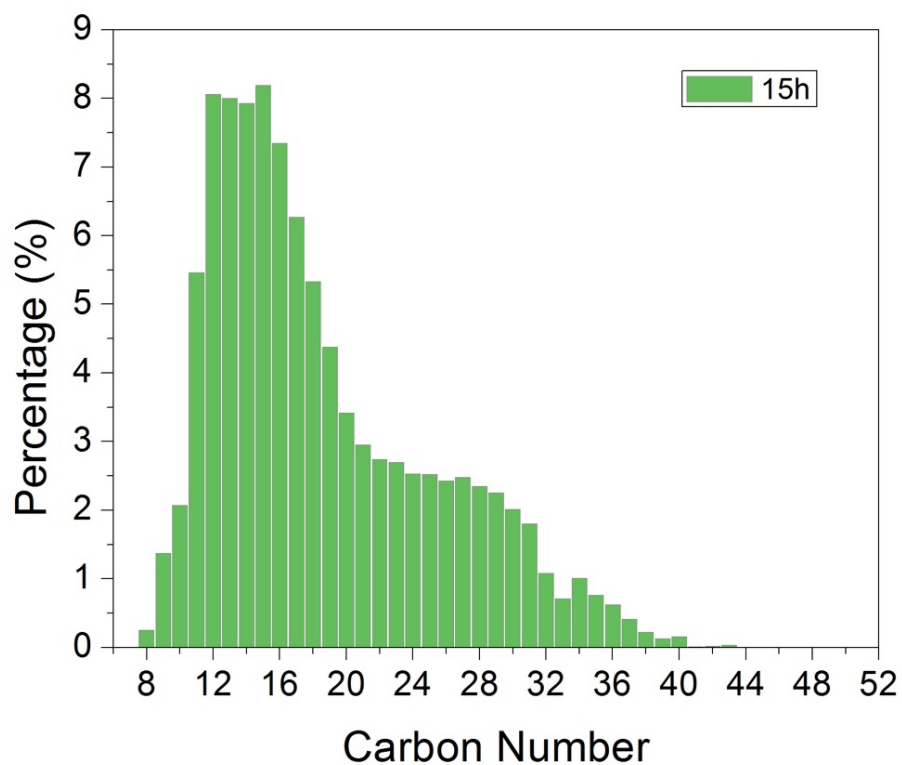
Supplementary Figure 64. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-6/mSiO}_2$, yielding 13.7% volatile species with respect to the mass of the starting PE (Supplementary Table 4). Conditions: 0.0119 ZrO_2 wt / PE wt %, 15 h, 300 °C, under H_2 (0.992 MPa).



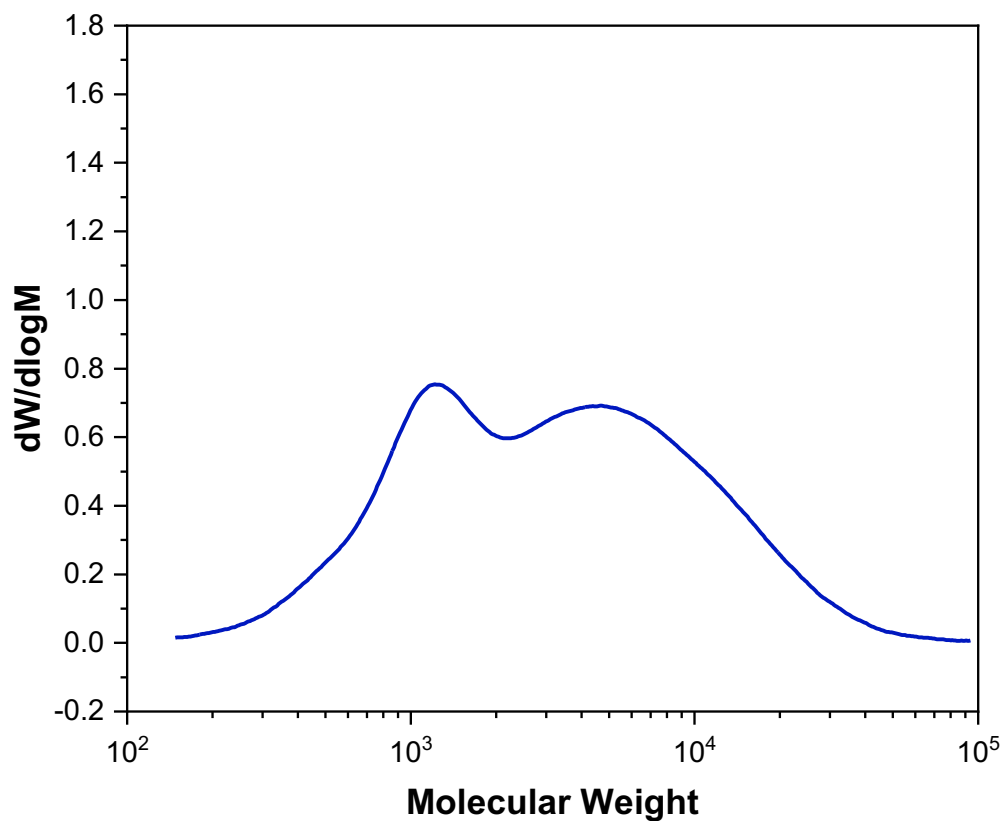
Supplementary Figure 65. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 64) of the sampled headspace from the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-6/mSiO}_2$. Conditions: 0.0119 ZrO_2 wt / PE wt %, 15 h, 300 °C, under H_2 (0.992 MPa).



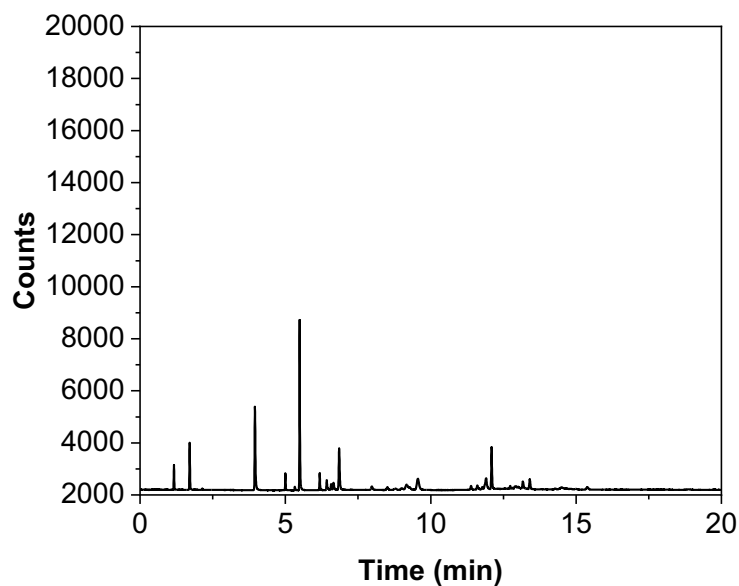
Supplementary Figure 66. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by ZrO₂-6/mSiO₂ (Supplementary Table 4). Conditions: 0.0119 ZrO₂ wt / PE wt %, 15 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 25.1% of the mass of the starting PE.



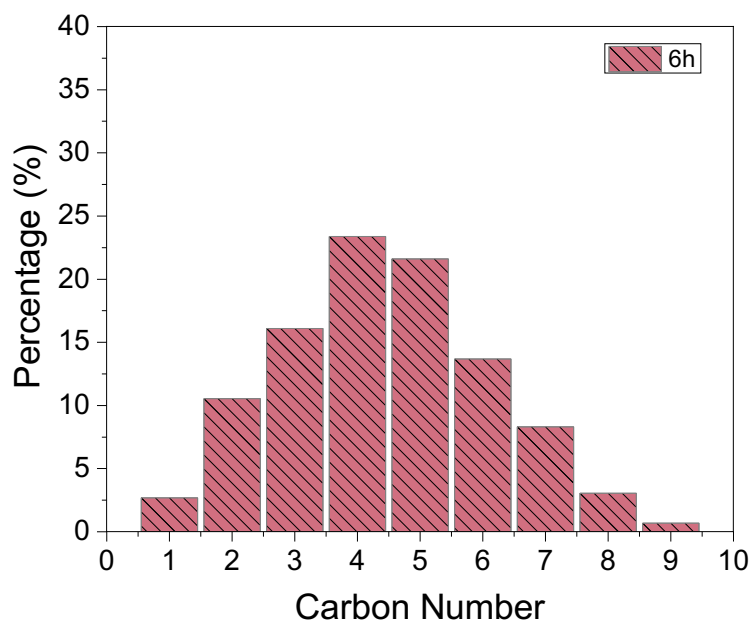
Supplementary Figure 67. Carbon number distribution determined from GC-MS analysis (Supplementary Figure 66) of the oil products from the hydrogenolysis of PE catalyzed by ZrO₂-6/mSiO₂. Conditions: 0.0119 ZrO₂ wt / PE wt %, 15 h, 300 °C, under H₂ (0.992 MPa).



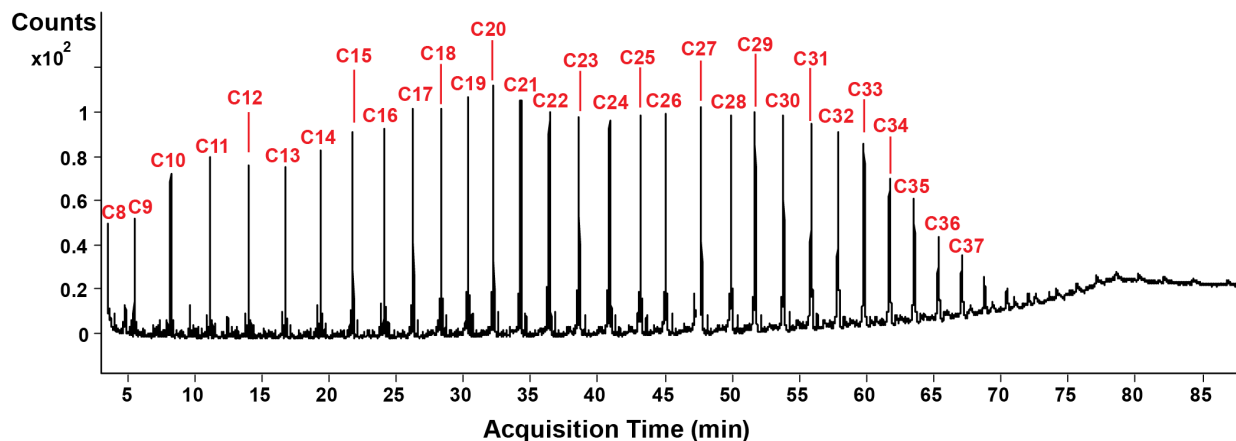
Supplementary Figure 68. GPC trace of the solid remaining after the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-6/mSiO}_2$ and extraction of soluble oils with methylene chloride, yielding 61.0 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.0119 ZrO_2 wt / PE wt %, 15 h, 300 °C, under H_2 (0.992 MPa). $M_n = 1,700$ Da, $M_w = 5,800$ Da, $\bar{D} = 3.4$ (Supplementary Table 7).



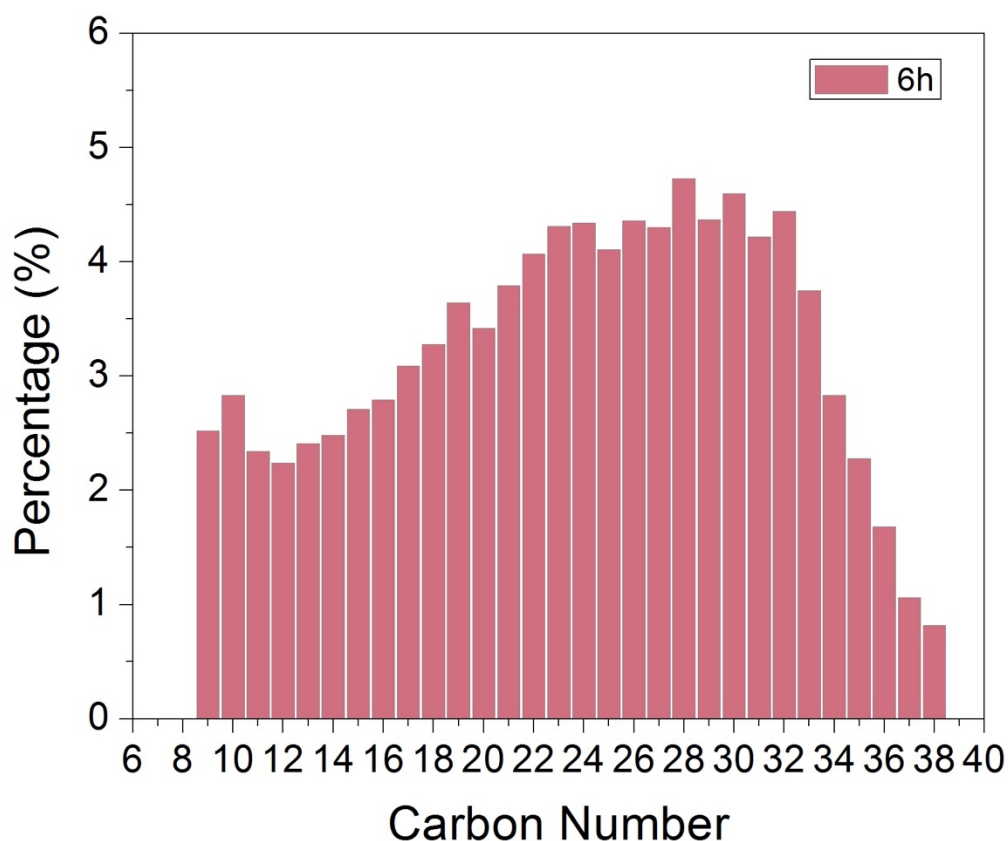
Supplementary Figure 69. GC-FID trace of the sampled headspace for the hydrogenolysis of PE catalyzed by ZrO₂-30, yielding 0.7% volatile species with respect to the mass of the starting PE (Supplementary Table 4). Conditions: 0.183 ZrO₂ wt / PE wt %, 6 h, at 300 °C, under H₂ (0.992 MPa).



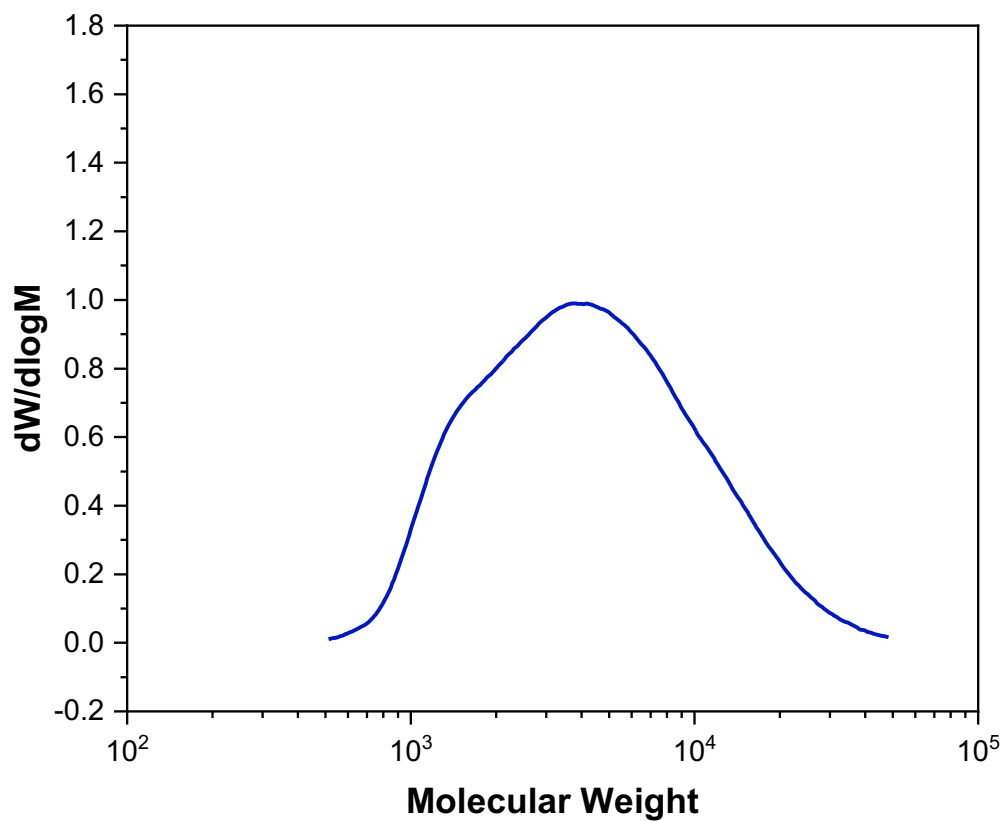
Supplementary Figure 70. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 69) of the sampled headspace from the hydrogenolysis of PE catalyzed by ZrO₂-30. Conditions: 0.183 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



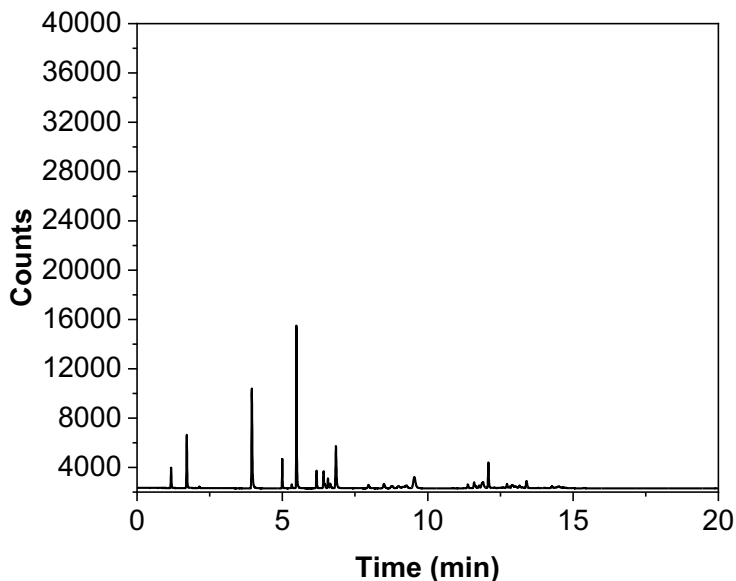
Supplementary Figure 71. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-30}$. Conditions: 0.183 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 12.6% of the mass of the starting PE.



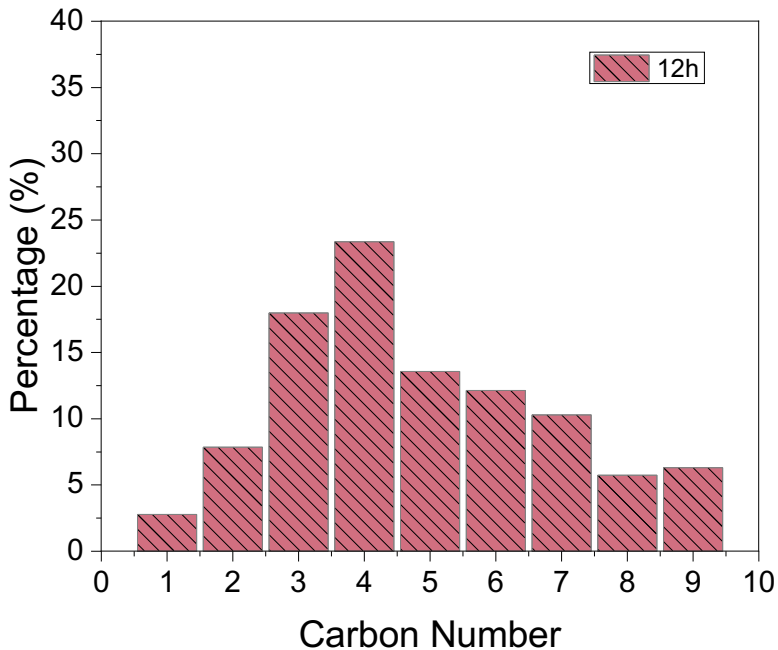
Supplementary Figure 72. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 71) of the oil products from the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-30}$. Conditions: 0.183 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa).



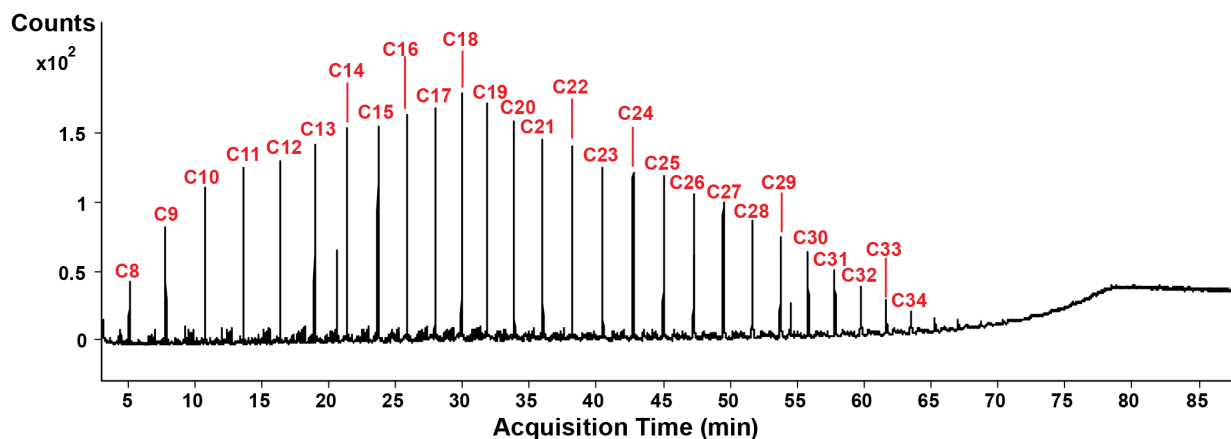
Supplementary Figure 73. GPC trace of the solid remaining after the hydrogenolysis of PE catalyzed by $\text{ZrO}_2\text{-30}$ and extraction of the soluble oils using methylene chloride, yielding 86.7 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.183 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa). $M_n = 3,000$ Da, $M_w = 6,000$ Da, $D = 2.0$ (Supplementary Table 7).



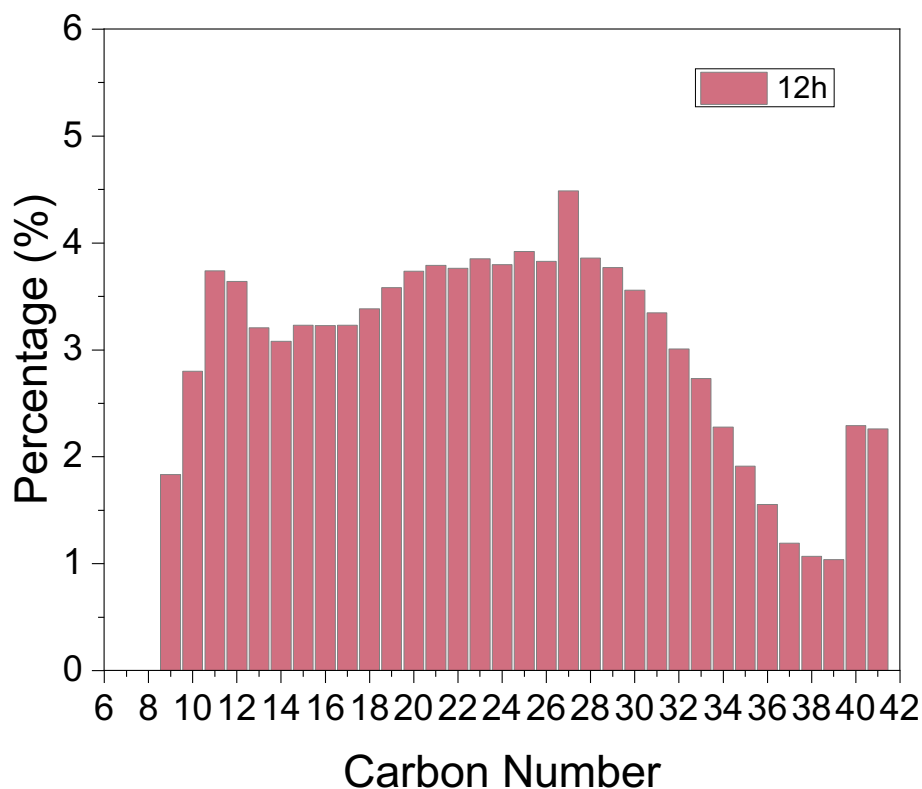
Supplementary Figure 74. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by ZrO₂-30, yielding 3.3% volatile species with respect to the mass of the starting PE (Supplementary Table 4). Conditions: 0.183 ZrO₂ wt / PE wt %, 12 h, 300 °C, under H₂ (0.992 MPa).



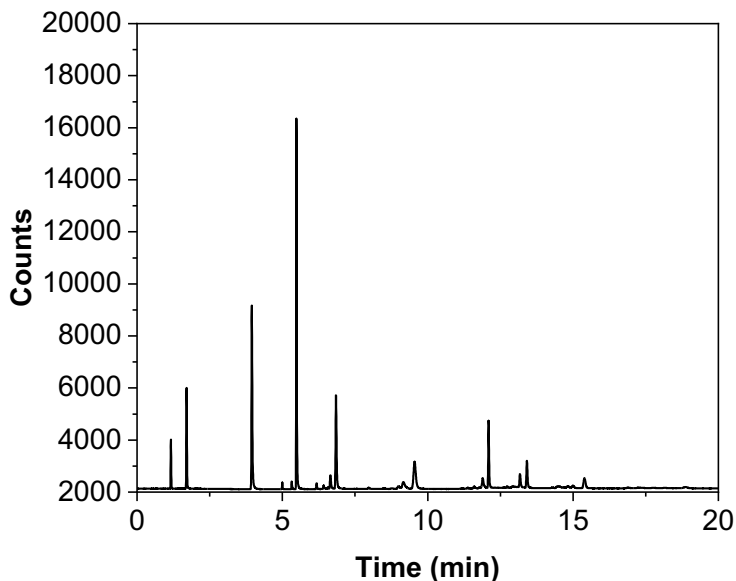
Supplementary Figure 75. Carbon number distribution determined from GC-FID analysis (Supplementary Figure 74) of the sampled headspace from the hydrogenolysis of PE catalyzed by ZrO₂-30. Conditions: 0.183 ZrO₂ wt / PE wt %, 12 h, 300 °C, under H₂ (0.992 MPa).



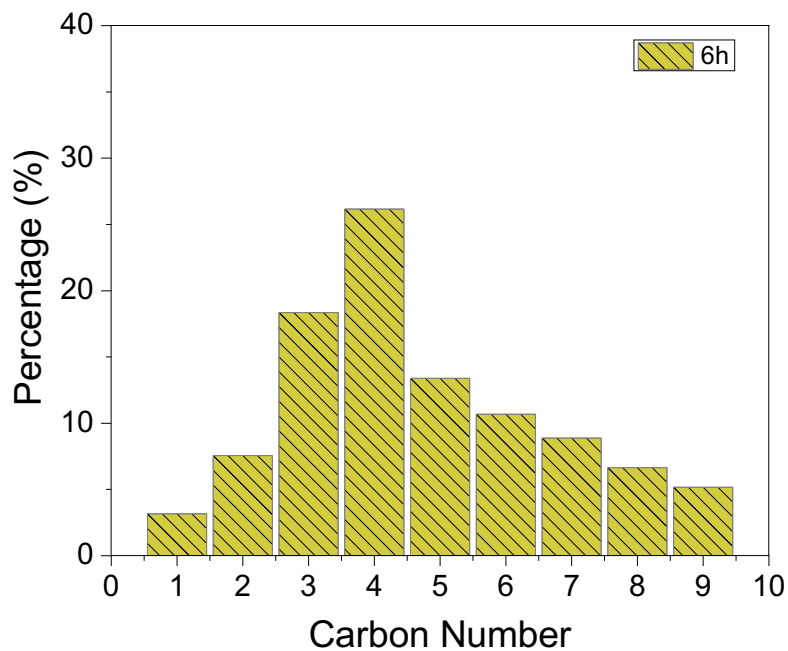
Supplementary Figure 76. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by ZrO₂-30 (Supplementary Table 4). Conditions: 0.183 ZrO₂ wt / PE wt %, 12 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 27.7% of the mass of the starting PE.



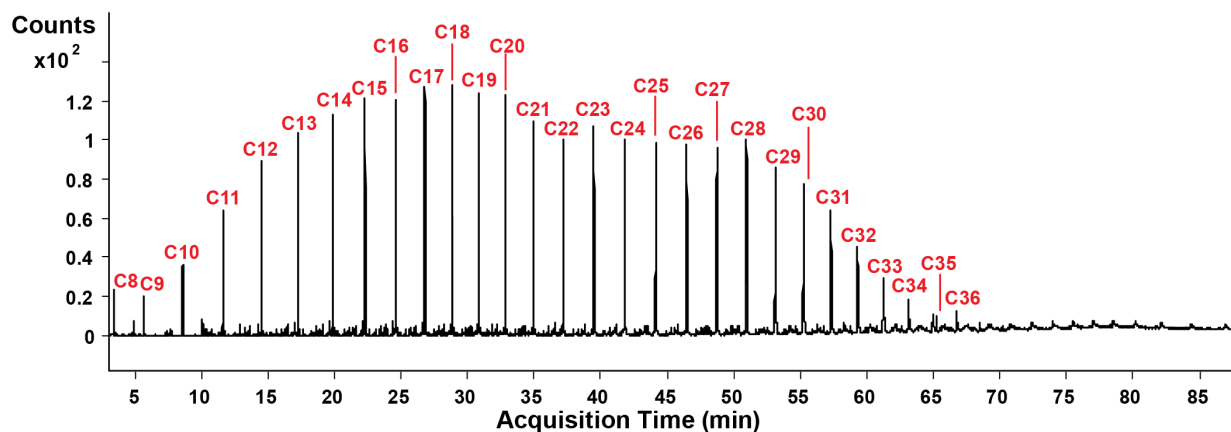
Supplementary Figure 77. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 76) of the oil products from the hydrogenolysis of PE catalyzed by ZrO₂-30. Conditions: 0.183 ZrO₂ wt / PE wt %, 12 h, 300 °C, under H₂ (0.992 MPa).



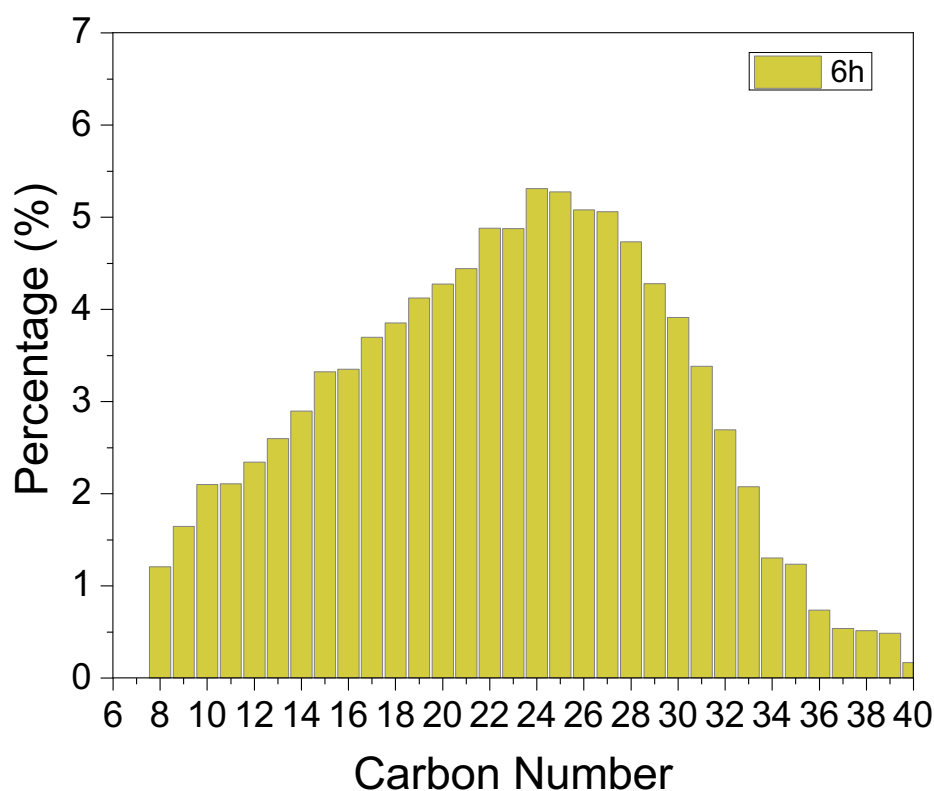
Supplementary Figure 78. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by L-Pt@mSiO₂, yielding 2.6% volatile species with respect to the mass of the starting PE (Supplementary Table 4). Conditions: 0.0092 Pt wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



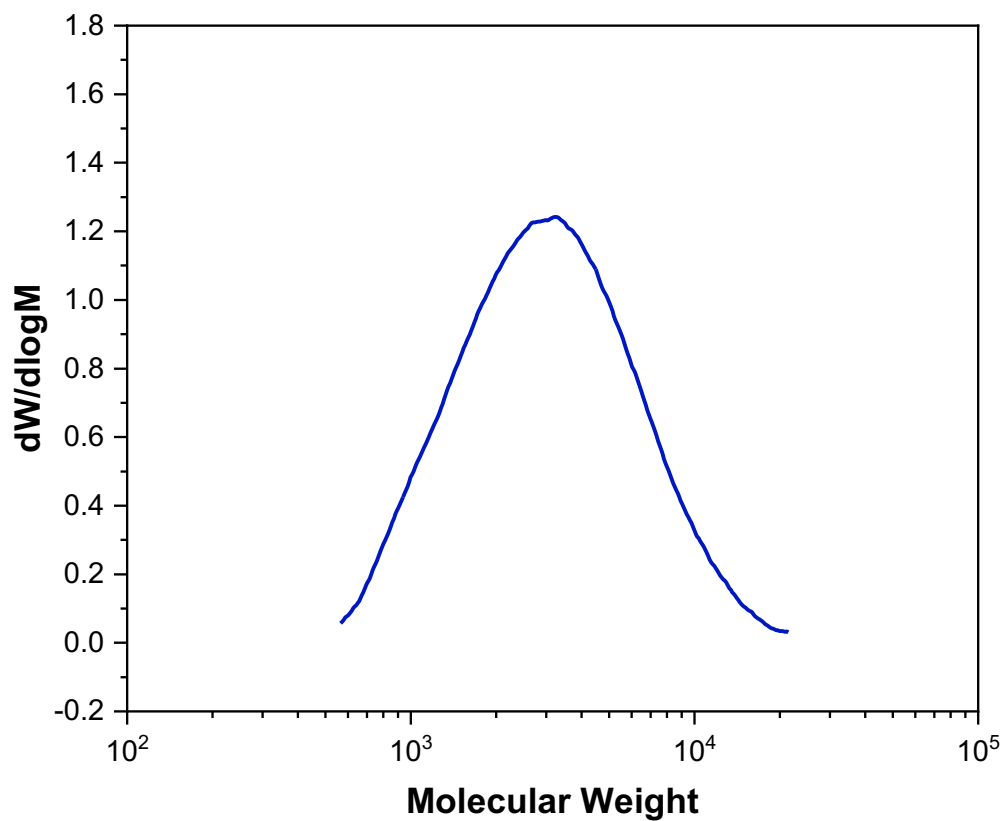
Supplementary Figure 79. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 78) of the sampled headspace from the hydrogenolysis of PE catalyzed by L-Pt@mSiO₂. Conditions: 0.0092 Pt wt / PE wt %, 6 h, 300 °C under H₂ (0.992 MPa).



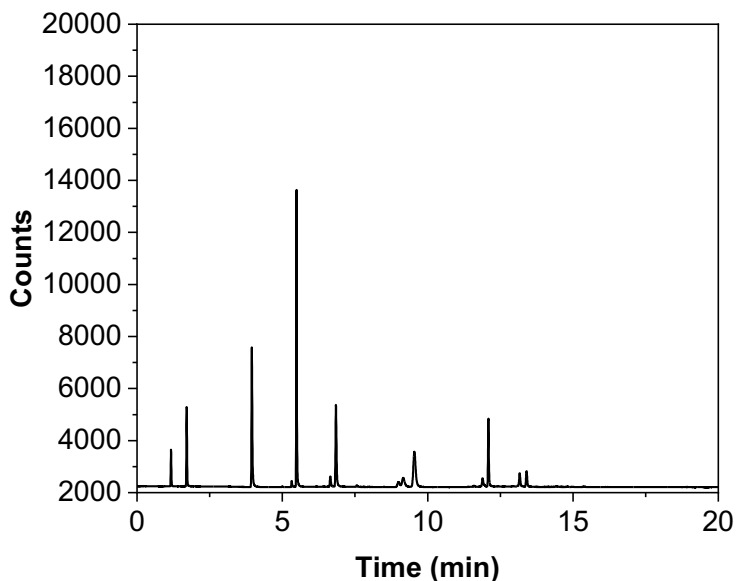
Supplementary Figure 80. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by L-Pt@mSiO₂. Conditions: 0.0092 Pt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 51.5% of the mass of the starting PE (Supplementary Table 4).



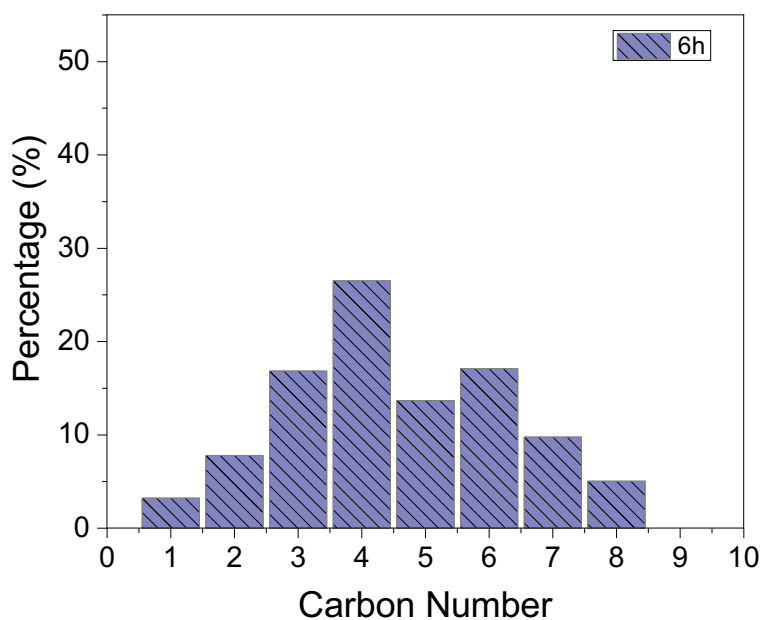
Supplementary Figure 81. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 80) of the oil products from the hydrogenolysis of PE catalyzed by L-Pt@mSiO₂. Conditions: 0.0092 Pt wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



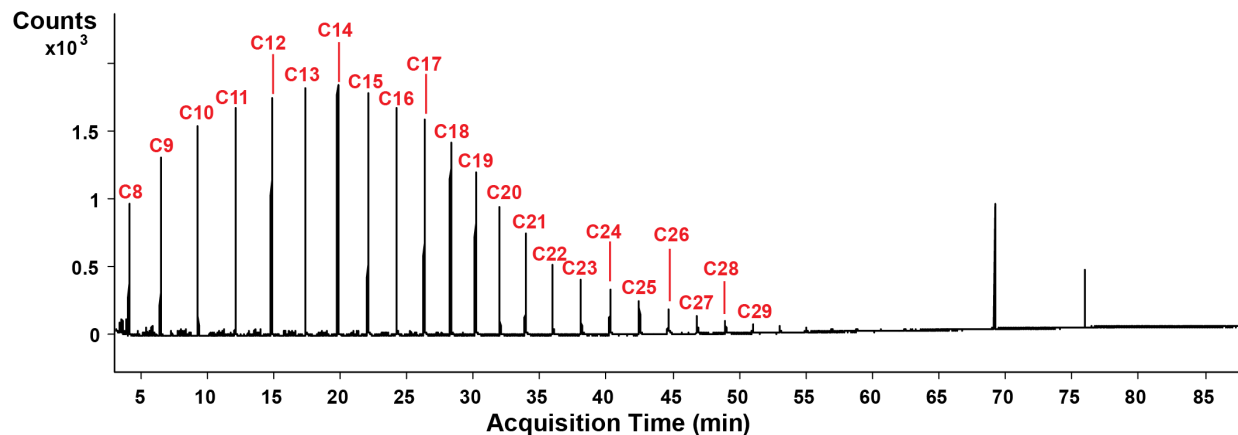
Supplementary Figure 82. GPC trace of the solid remaining after hydrogenolysis of PE catalyzed by L-Pt@mSiO₂ and extraction of soluble oils using methylene chloride, yielding 45.9 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.0092 Pt wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). $M_n = 2,400$ Da, $M_w = 3,800$ Da, $\bar{D} = 1.6$ (Supplementary Table 7).



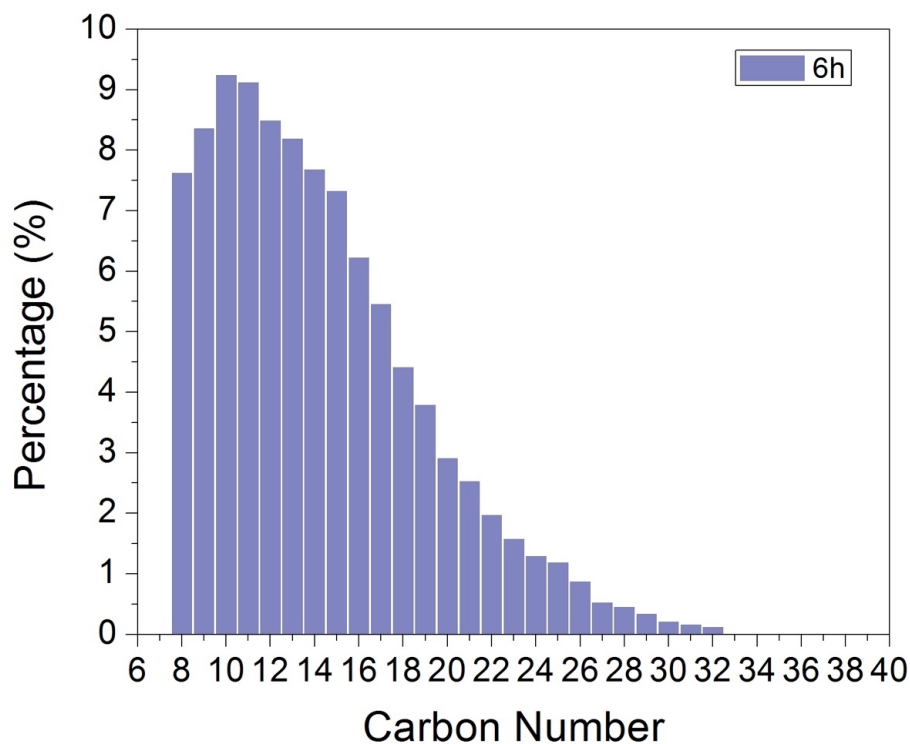
Supplementary Figure 83. GC-FID trace of the sampled headspace from the hydrogenolysis of PE catalyzed by Pt/C, yielding 2.2% volatile species with respect to the mass of the starting PE (Supplementary Table 4). Conditions: 0.0092 Pt wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



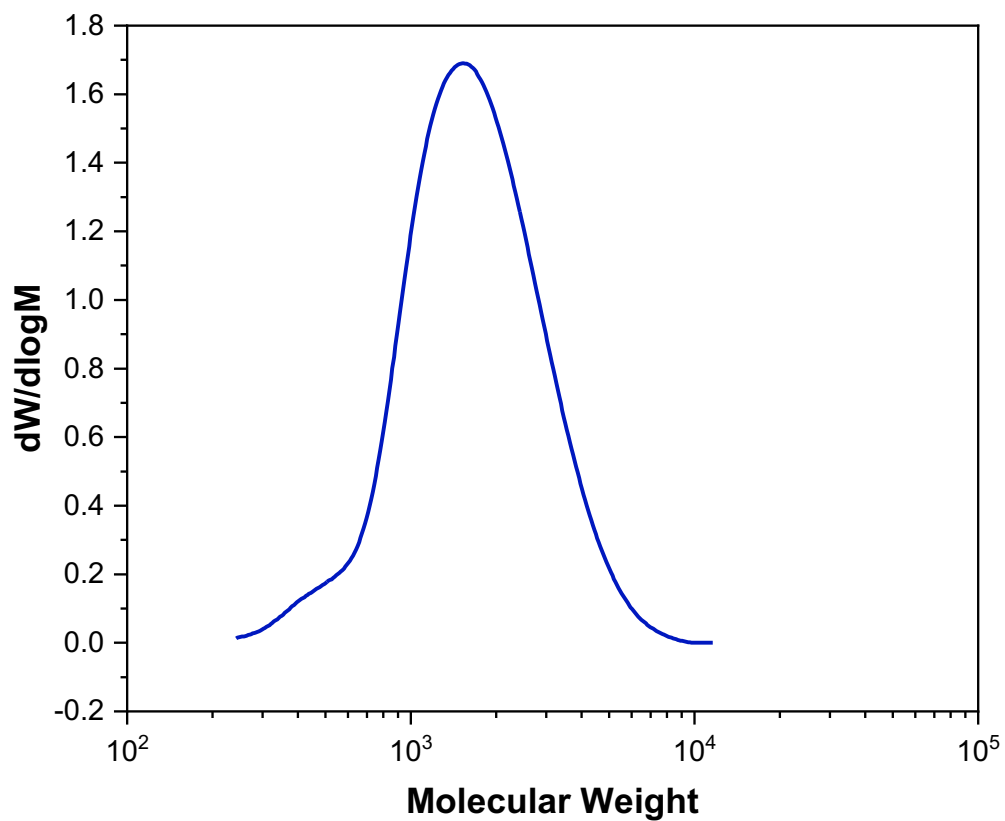
Supplementary Figure 84. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 83) of the sampled headspace from the hydrogenolysis of PE catalyzed by Pt/C. Conditions: 0.0092 Pt wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



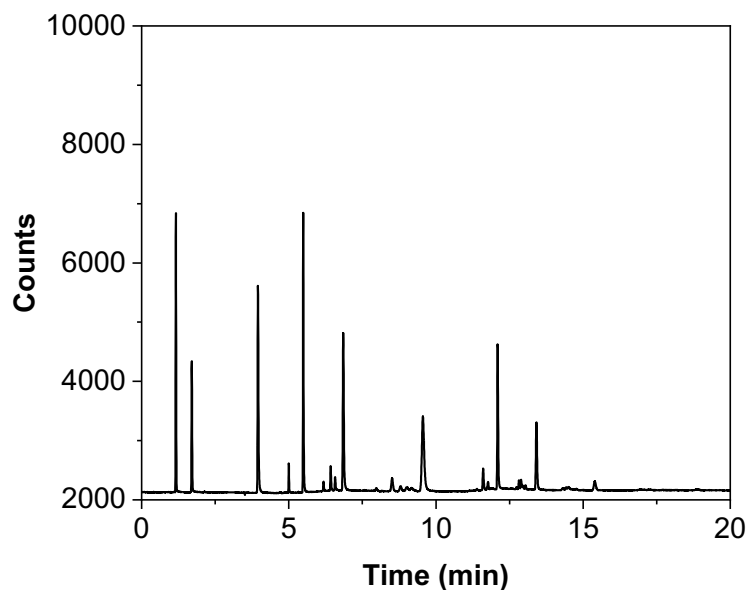
Supplementary Figure 85. GC-MS trace of the oil products from the hydrogenolysis of PE catalyzed by Pt/C. Conditions: 0.0092 Pt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 22.2% of the mass of the starting PE (Supplementary Table 4).



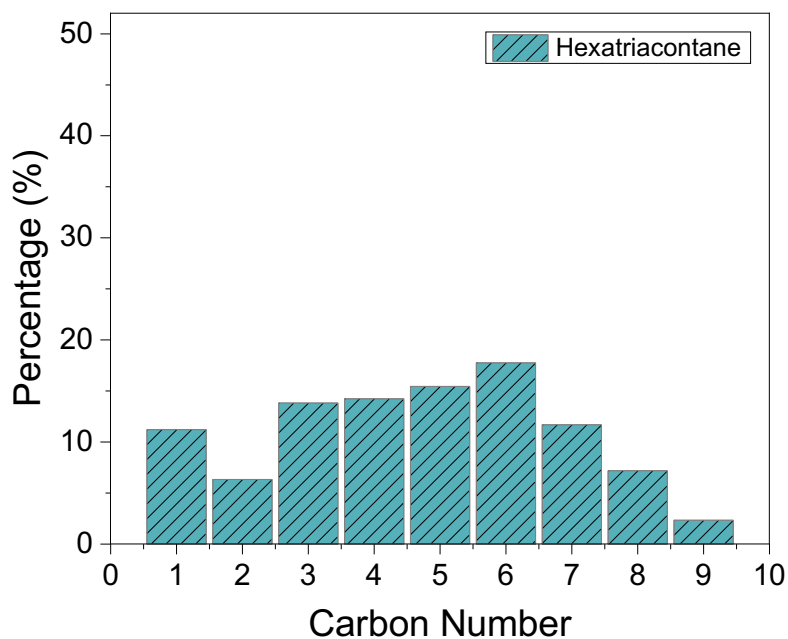
Supplementary Figure 86. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 85) of the oil products from the hydrogenolysis of PE catalyzed by Pt/C. Conditions: 0.0092 Pt wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



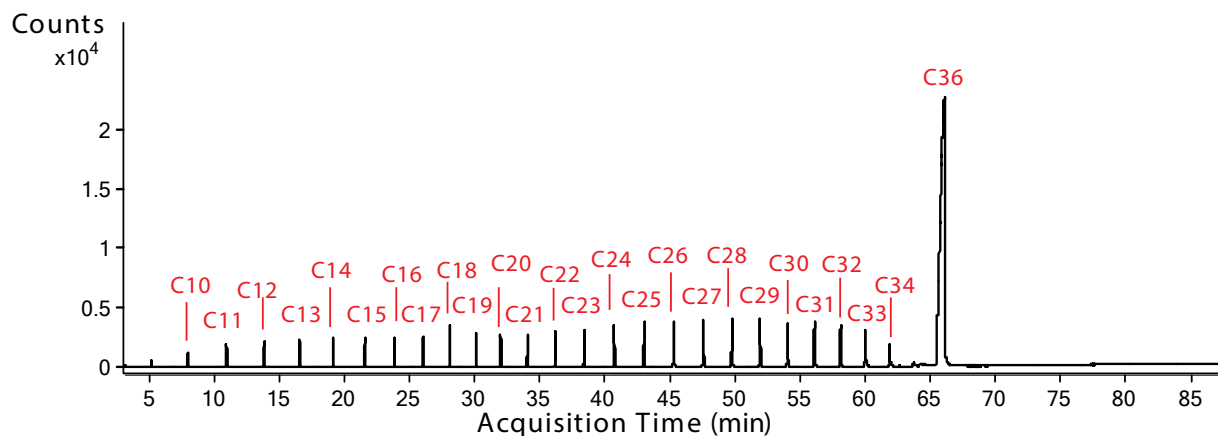
Supplementary Figure 87. GPC trace of the solid remaining after hydrogenolysis of PE catalyzed by Pt/C and extraction of soluble oils with methylene chloride, yielding 75.6 wt % solid residue with respect to the mass of the starting PE. Reaction conditions: 0.0092 Pt wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). $M_n = 1,400$ Da, $M_w = 1,900$ Da, $D = 1.4$ (Supplementary Table 7).



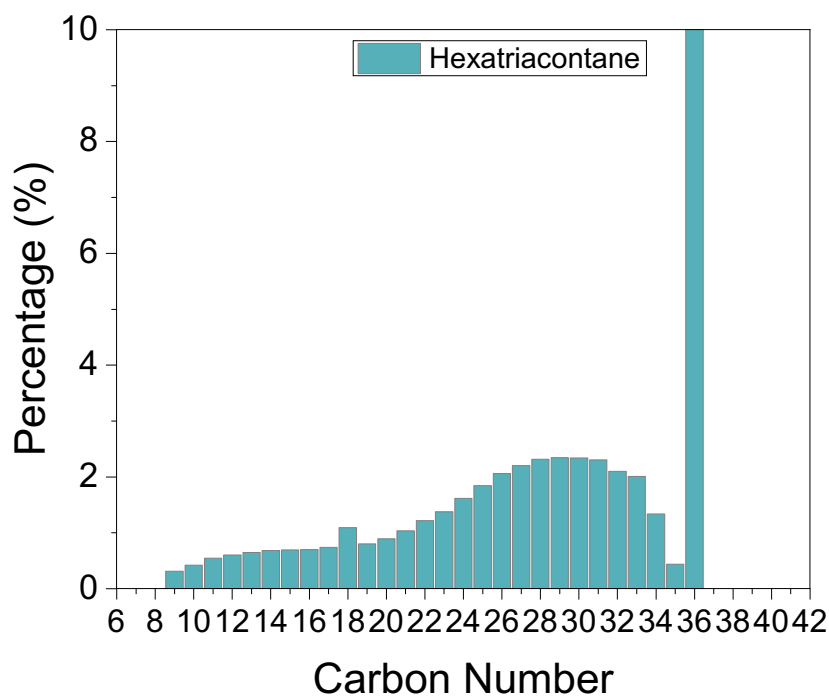
Supplementary Figure 88. GC-FID trace of the sampled headspace from the hydrogenolysis of hexatriacontane ($C_{36}H_{74}$) catalyzed by $L-ZrO_2@SiO_2$, yielding 1.7 wt % volatile species with respect to the mass of the hexatriacontane (Supplementary Table 5). Reaction conditions: 0.0086 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa).



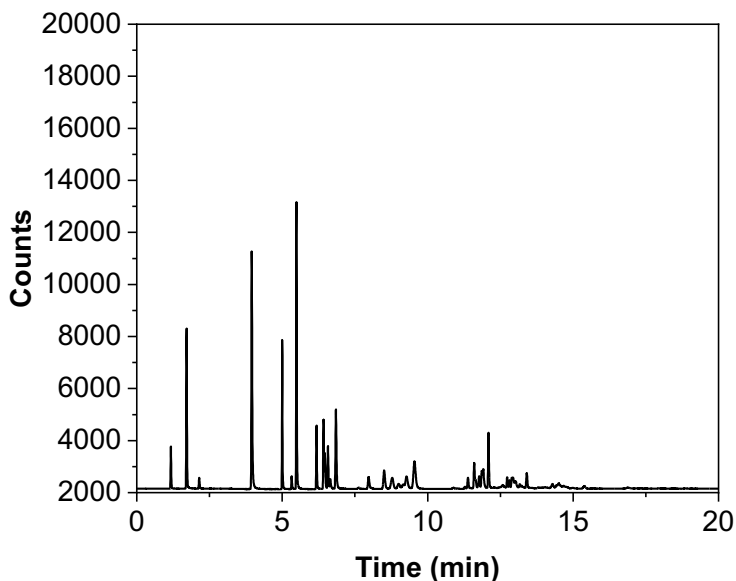
Supplementary Figure 89. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 88) of the sampled headspace from the hydrogenolysis of hexatriacontane catalyzed by $L-ZrO_2@SiO_2$. Conditions: 0.0086 ZrO_2 wt / PE wt %, 6 h, 300 °C, under H_2 (0.992 MPa).



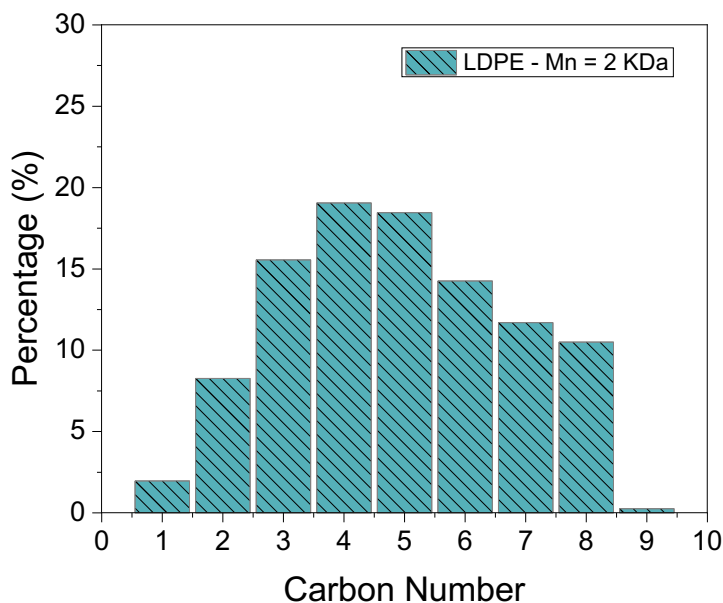
Supplementary Figure 90. GC-MS trace of the oil products from the hydrogenolysis of hexatriacontane catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). Workup: Solid/liquid mixture was scraped from the reaction vessel. 34% of the starting hexatriacontane was converted.



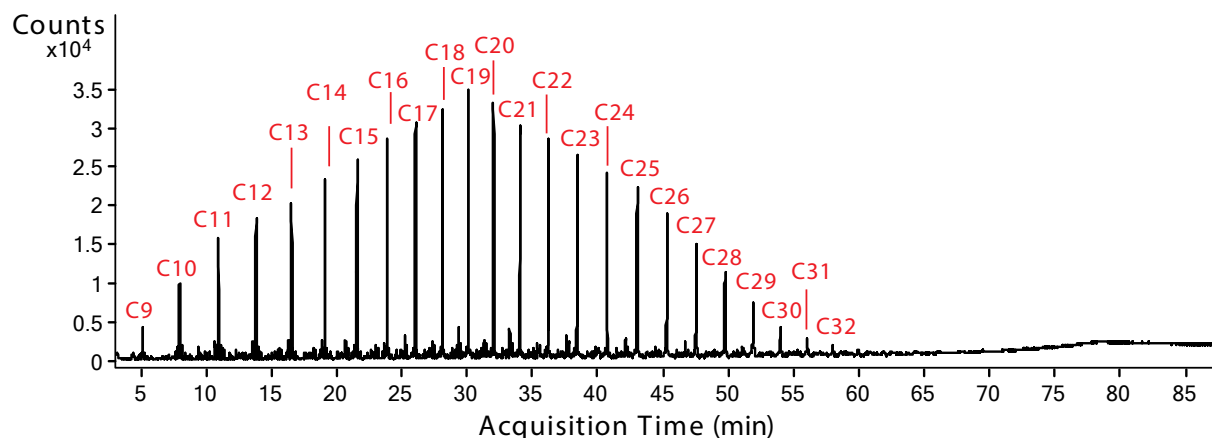
Supplementary Figure 91. Carbon number distribution determined from GC-MS analysis (Supplementary Figure 90) of the oil products from the hydrogenolysis of PE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



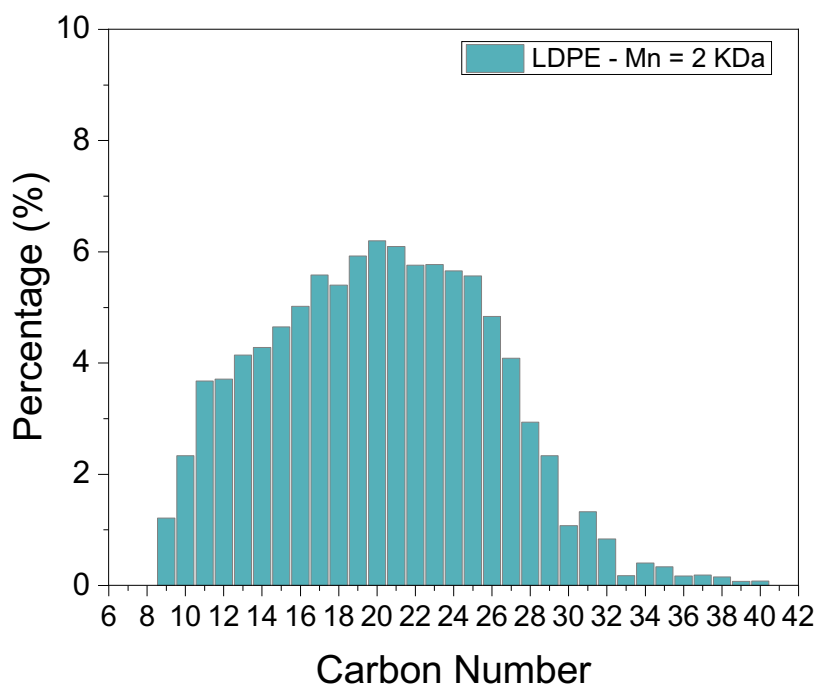
Supplementary Figure 92. GC-FID trace of the sampled headspace from the hydrogenolysis of LDPE ($M_n = 2.8$ kDa, $M_w = 5.3$ kDa) catalyzed by L-ZrO₂@SiO₂, yielding 4.5 wt % volatile species with respect to the mass of the starting PE (Supplementary Table 5). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



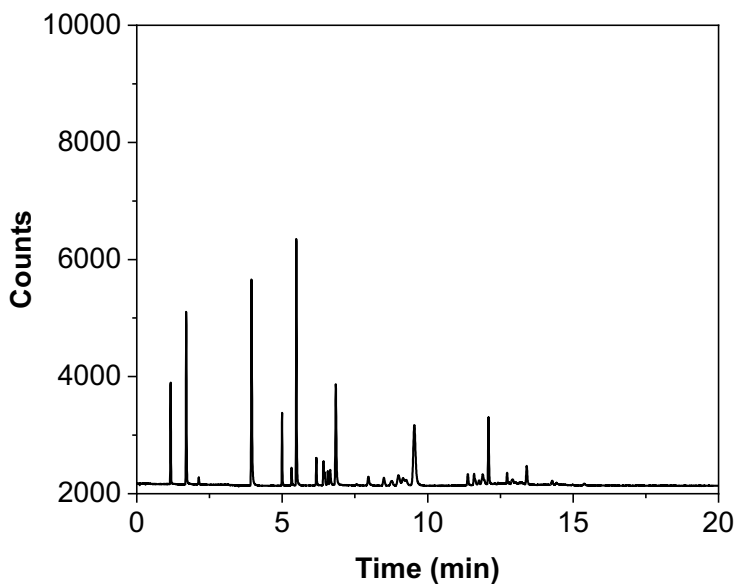
Supplementary Figure 93. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 92) of the sampled headspace from the hydrogenolysis of LDPE ($M_n = 2.8$ kDa, $M_w = 5.3$ kDa) catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



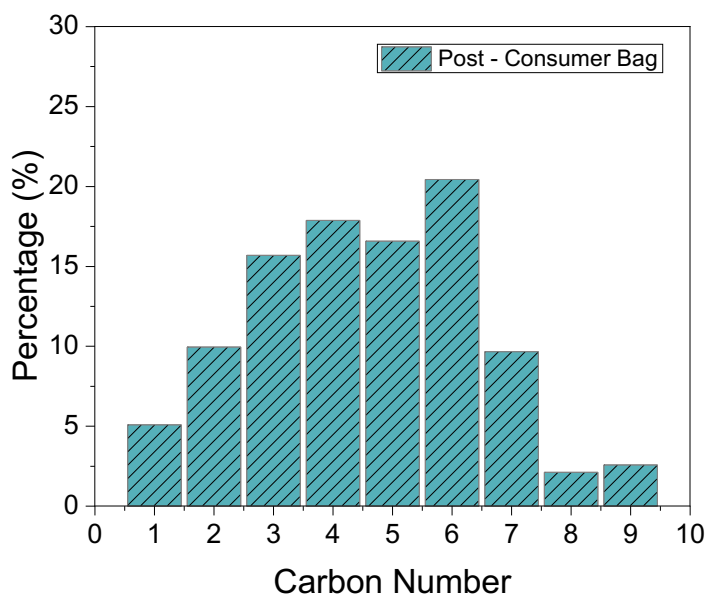
Supplementary Figure 94. GC-MS trace of the oil products from the hydrogenolysis of LDPE ($M_n = 2.8$ kDa, $M_w = 5.3$ kDa) catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 47.4 % of the mass of the starting PE.



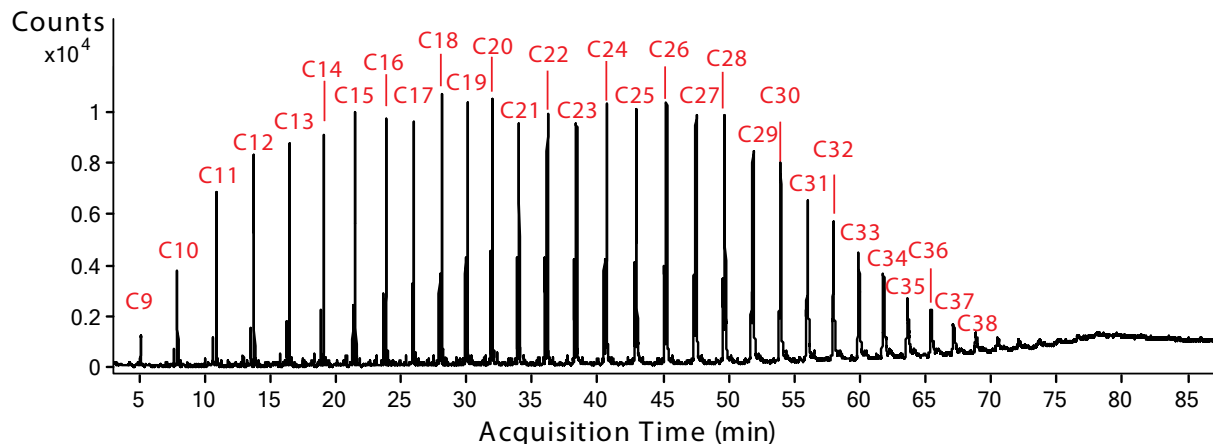
Supplementary Figure 95. Carbon number distribution of the oil products from the hydrogenolysis of LDPE ($M_n = 2.8$ kDa, $M_w = 5.3$ kDa) catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



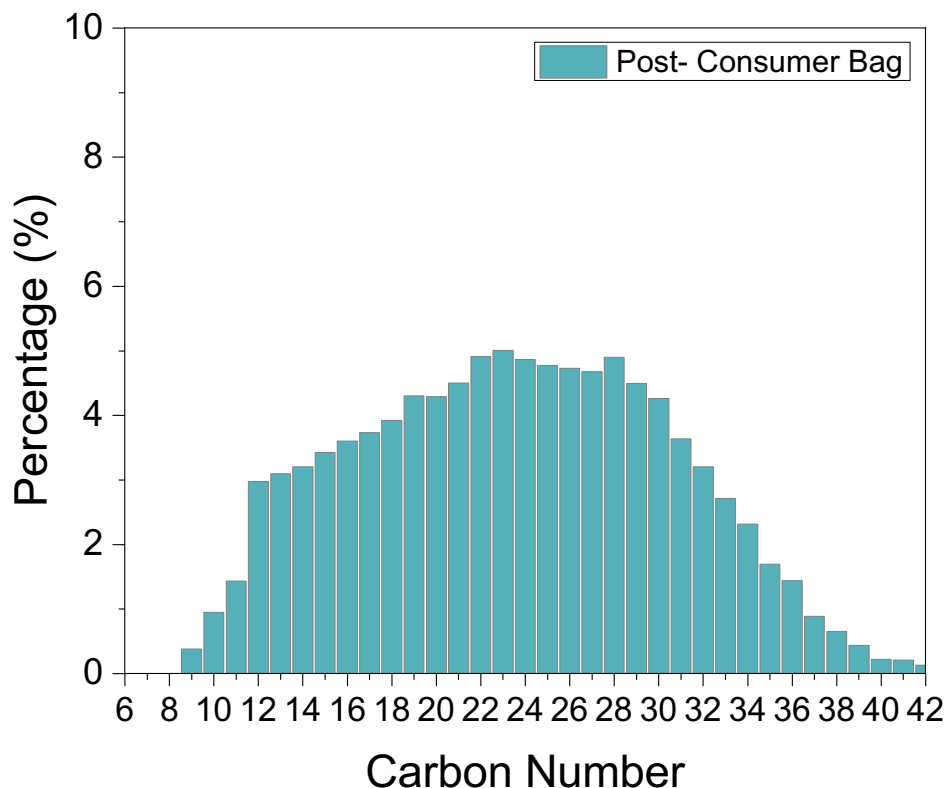
Supplementary Figure 96. GC-FID trace of the sampled headspace from the hydrogenolysis of a post-consumer grocery bag catalyzed by L-ZrO₂@SiO₂, yielding 1.7 wt % volatile species with respect to the mass of the starting PE (Supplementary Table 5). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



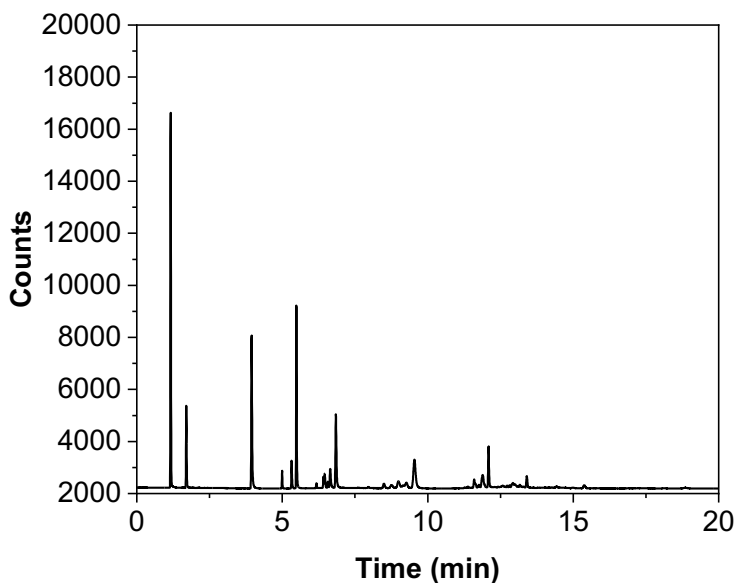
Supplementary Figure 97. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 96) of the sampled headspace from the hydrogenolysis of a post-consumer grocery bag catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



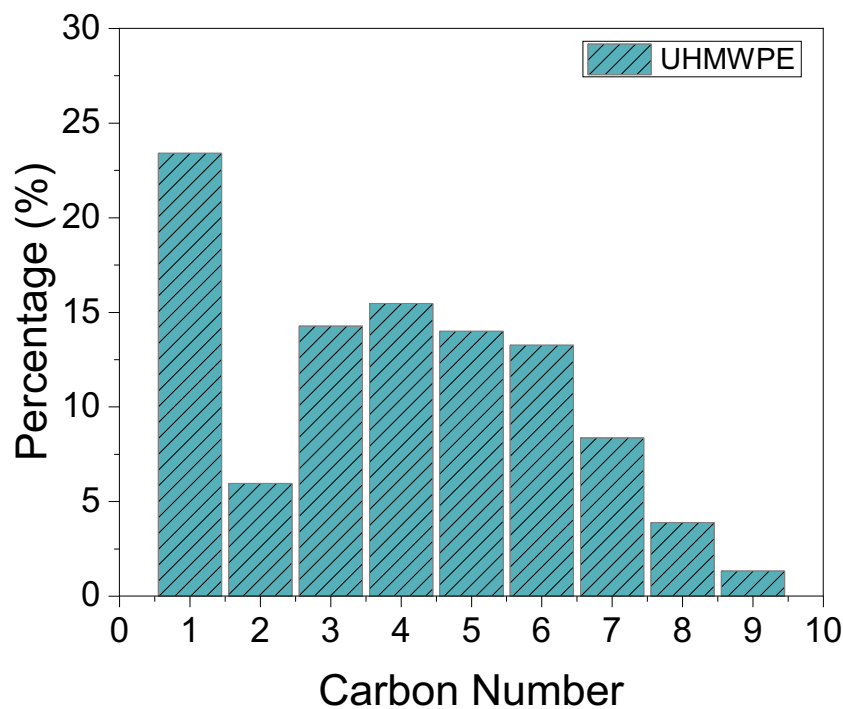
Supplementary Figure 98. GC-MS trace of the oil products from the hydrogenolysis of post-consumer grocery bag catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 41.1% of the mass of the starting PE (Supplementary Table 5).



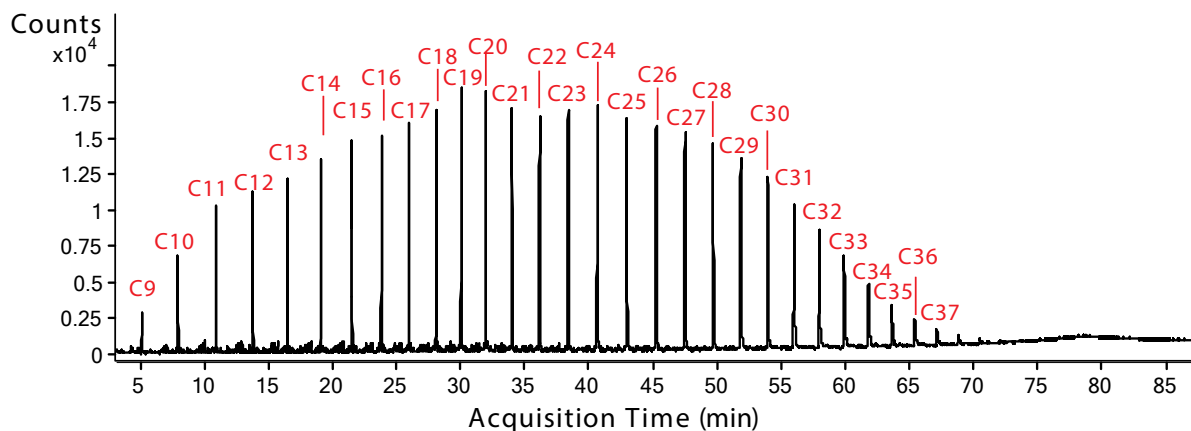
Supplementary Figure 99. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 98) of the oil products from the hydrogenolysis of post-consumer grocery bag catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



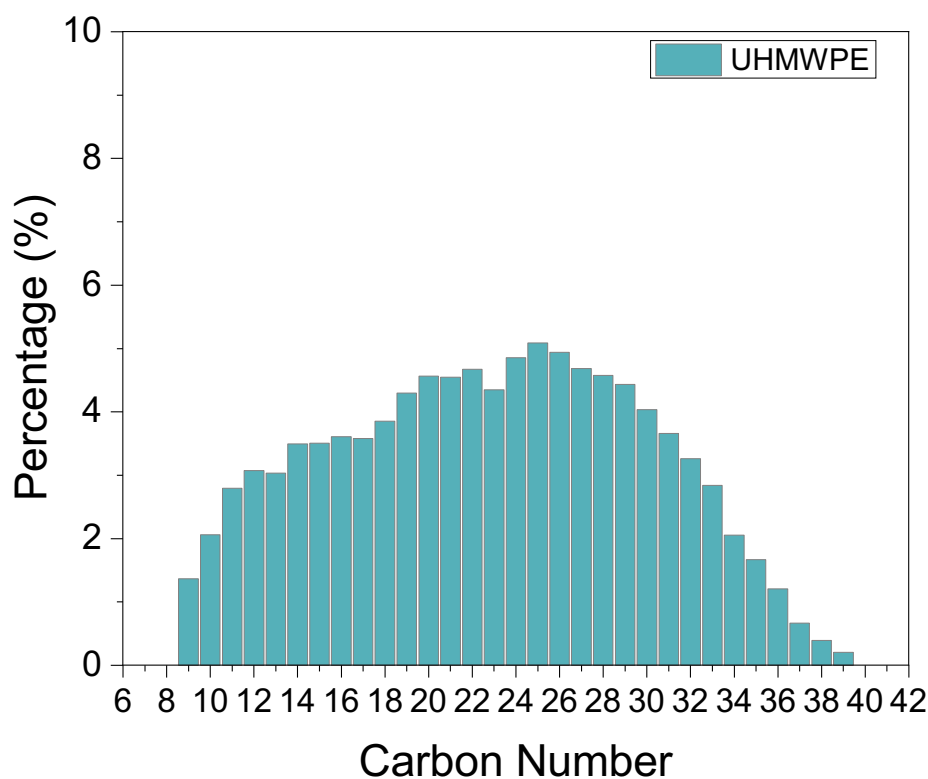
Supplementary Figure 100. GC-FID trace of the sampled headspace from the hydrogenolysis of UHMWPE catalyzed by L-ZrO₂@SiO₂, yielding 2.9 wt % volatile species with respect to the mass of the starting PE (Supplementary Table 5). Reaction conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



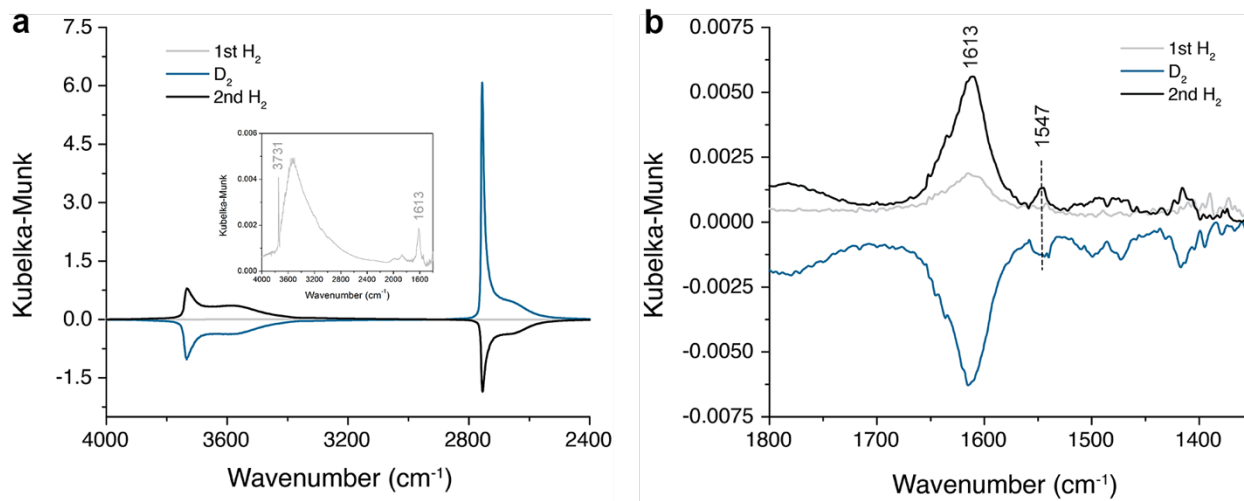
Supplementary Figure 101. Carbon number distribution determined by GC-FID analysis (Supplementary Figure 100) of the sampled headspace from the hydrogenolysis of UHMWPE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



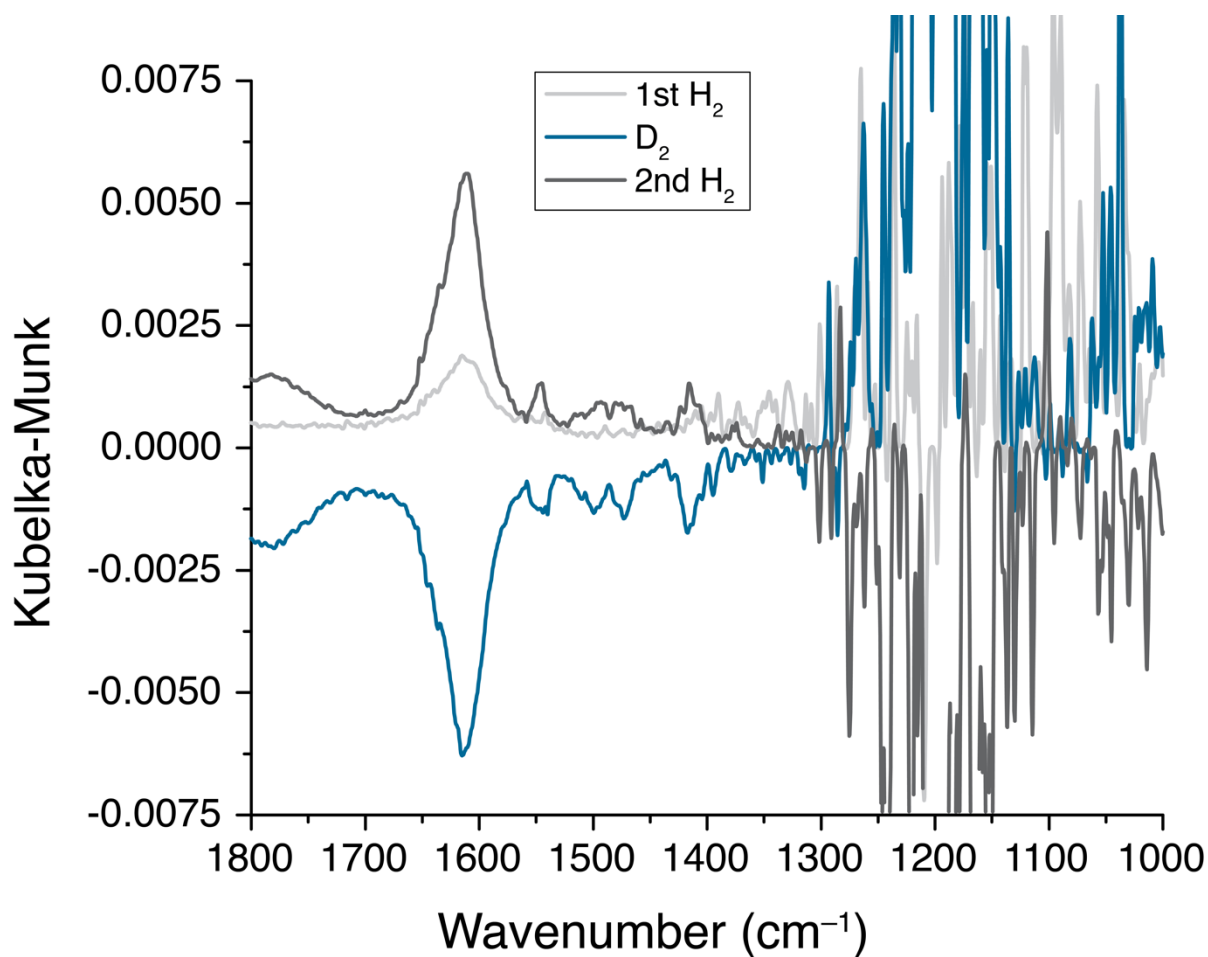
Supplementary Figure 102. GC-MS trace of the oil products from the hydrogenolysis of UHMWPE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa). Workup: extraction of the solid reaction mixture with methylene chloride at 80 °C. Oil yield corresponds to 46.6% of the mass of the starting PE (Supplementary Table 5).



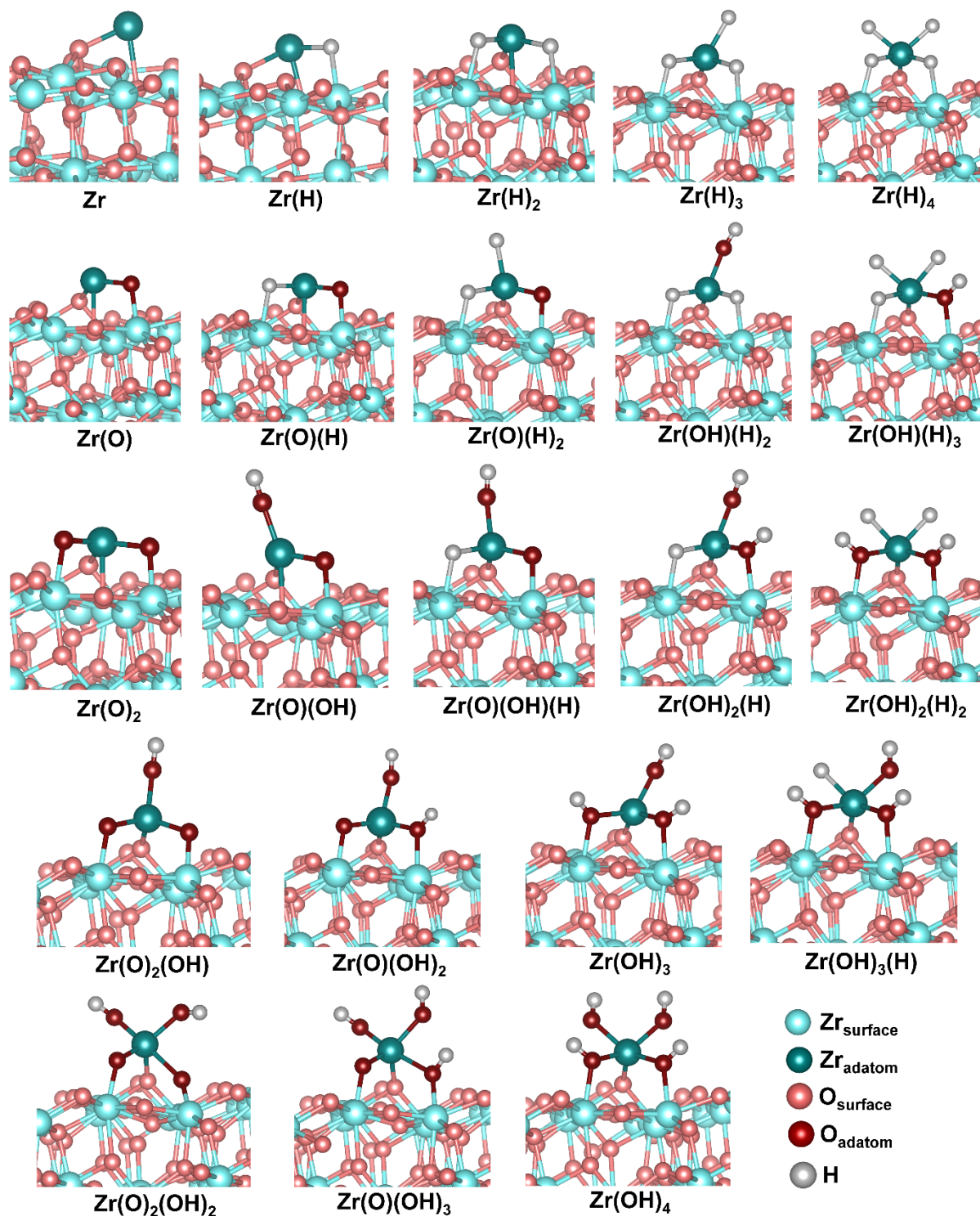
Supplementary Figure 103. Carbon number distribution determined by GC-MS analysis (Supplementary Figure 102) of the oil products from the hydrogenolysis of UHMWPE catalyzed by L-ZrO₂@SiO₂. Conditions: 0.0086 ZrO₂ wt / PE wt %, 6 h, 300 °C, under H₂ (0.992 MPa).



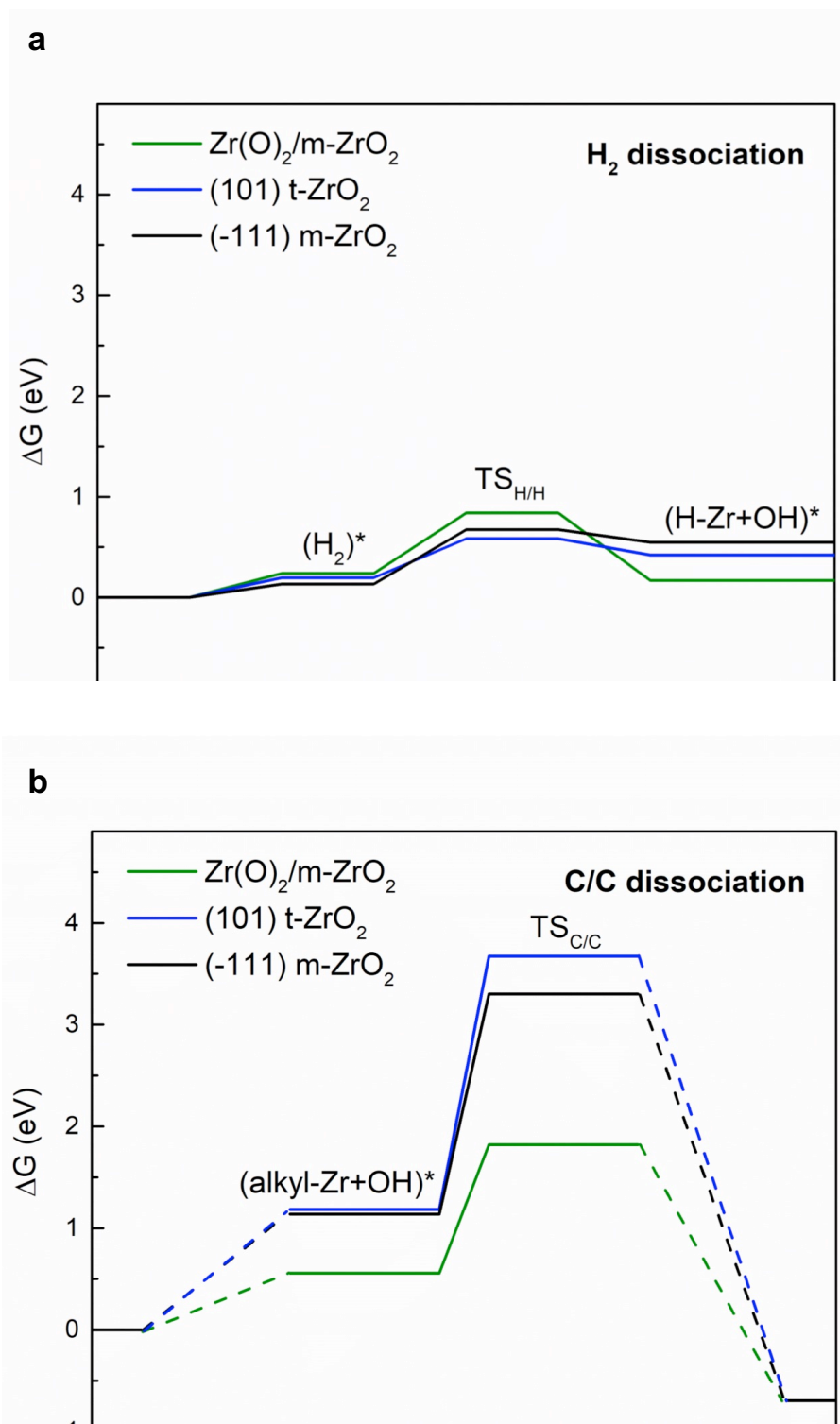
Supplementary Figure 104. DRIFTS spectra of L-ZrO₂@mSiO₂ under H₂ and D₂ gas flow at 300 °C: a) in the range of 4000 – 2400 cm^{-1} (inset: enlarged of the spectrum under 1st H₂ flow) and b) in the range of 1800 – 1350 cm^{-1} .



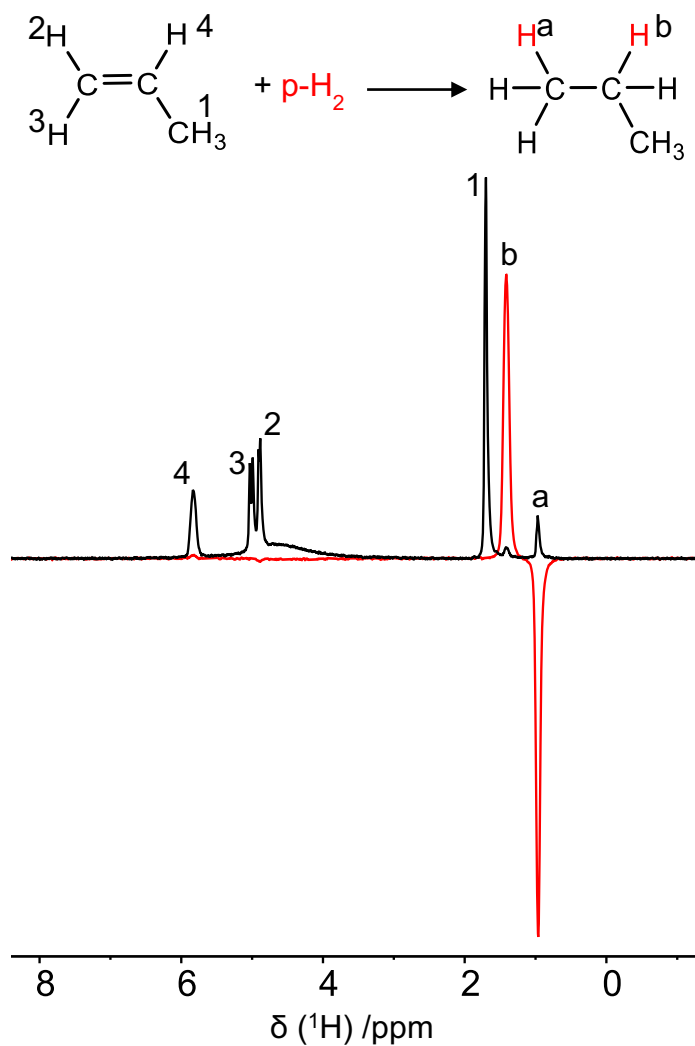
Supplementary Figure 105. DRIFTS spectra of L-ZrO₂@mSiO₂ under H₂ and D₂ gas flow at 300 °C in the range of 1800 – 1000 cm⁻¹. Zr–D stretch at about 1100 cm⁻¹ is not observed due to the strong sample absorption from 1300 to 1000 cm⁻¹.



Supplementary Figure 106. Side view of the most stable geometries calculated for ZrO_xH_y supported on m- ZrO_2 (-111).



Supplementary Figure 107. Comparison of free energies of (a) H_2 activation and (b) C–C bond cleavage transition states involved in n-hexane hydrogenolysis calculated over the flat m-ZrO_2 (-111) and t-ZrO_2 (101) surfaces as well as the low-coordinated $\text{Zr(O)}_2/\text{m-ZrO}_2$ active site models.



Supplementary Figure 108. The continuous flow ALTADENA spectrum (red) and the thermally polarized spectrum (black) in propene hydrogenation with 99% $p\text{-H}_2$ using $\text{L-ZrO}_2@\text{mSiO}_2$ catalysts at 300 °C. The total flow rate is 60 sccm, with a H_2 /propene ratio of 5/1.

Supplementary Tables

Supplementary Table 1. Source and some characteristics of catalysts studied in this work.

Entry	Catalyst	Source	Catalyst Loading [wt.%]	SSA _{BET} [m ² /g]	<i>D</i> _{pore} [nm] ^d
1	mSiO ₂	Syn. ^a	0.0	1022	3.6
2	L-ZrO ₂ @mSiO ₂	Syn. ^a	4.7	973	3.7
3	imp-ZrO ₂ /mSiO ₂	Syn. ^a	4.1	959	3.6
4	ZrO ₂ -6/mSiO ₂	Syn. ^a	6.0	966	3.8
5	ZrO ₂ -30	Aldrich ^b	100	37	n.a. ^c
6	L-Pt@mSiO ₂	Syn. ^a	3.6	909	3.4
7	Pt/C	Alfa Aesar ^c	7.1	n.a.	n.a.

^a Synthesized in this work. ^b Purchased from Aldrich. ^c Purchased from Alfa Aesar. ^d Pore size calculated from the desorption branch of nitrogen gas sorption isotherm using BJH method. ^e Not applicable.

Supplementary Table 2. Weight percentage of metal in ZrO₂-based catalytic materials, potentially present as trace impurities, calculated based on the inductively coupled plasma mass spectrometry (ICP-MS) analyses.^a

Metal	L-ZrO ₂ @mSiO ₂ _1	L-ZrO ₂ @mSiO ₂ _2	L-ZrO ₂ @mSiO ₂ _3	Spent L-ZrO ₂ @mSiO ₂ _3	ZrO ₂ -6 /mSiO ₂	imp-ZrO ₂ /mSiO ₂
Ru	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%
Rh	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%
Pd	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%
Pt	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%
Au	0.000%	0.000%	0.001%	0.000%	0.000%	0.000%
Re	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%
Ir	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%
Os	0.000%	0.000%	0.004%	0.000%	0.000%	0.000%
Fe	<0.000%	<0.000%	<0.000%	0.001%	<0.000%	<0.000%
Co	0.000%	0.000%	0.000%	0.001%	0.000%	0.000%
Ni	0.000%	0.000%	0.000%	<0.000%	0.000%	0.000%
Cu	0.000%	0.000%	0.000%	0.004%	0.003%	0.000%
Zn	0.002%	0.003%	<0.000%	<0.000%	<0.000%	<0.000%
Mo	0.000%	0.000%	<0.000%	0.010%	<0.000%	<0.000%
W	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%
Cd	0.000%	0.000%	0.000%	0.000%	0.000%	0.000%
Ce	0.001%	0.000%	<0.000%	<0.000%	<0.000%	<0.000%
Hf	0.000%	0.000%	<0.000%	<0.000%	<0.000%	<0.000%
Ti	0.000%	0.011%	<0.000%	<0.000%	<0.000%	<0.000%
V	0.000%	0.000%	<0.000%	<0.000%	<0.000%	<0.000%

^a L-ZrO₂@mSiO₂ was measured from three separately digested samples and labeled as L-ZrO₂@mSiO₂_1, L-ZrO₂@mSiO₂_2, and L-ZrO₂@mSiO₂_3.

Supplementary Table 3. Product compositions plotted in Figure 4a from the hydrogenolysis of PE over 2 – 20 h, catalyzed by L-ZrO₂@mSiO₂ under H₂ (0.992 MPa) at 300 °C.

Time (h)	PE (g)	Volatiles g (%)	Liquids g (%)	Solid residue g (%)	H₂ Consumption (mmol)
2	3.009	0.067 (2.2%)	0.467 (15.5%)	2.475 (82.3%)	1.8 ± 0.2
4	3.003	0.089 (3.0%)	0.835 (27.8%)	2.078 (69.2%)	3.1 ± 0.6
6	3.003	0.082 (2.7%)	1.257 (42.3%)	1.664 (55.4%)	3.6 ± 0.6
8	3.016	0.195 (6.47%)	1.659 (55.0%)	1.162 (38.5%)	5.2 ± 0.7
12	3.004	0.230 (7.7%)	1.951 (64.9%)	0.823 (27.4%)	8.1 ± 1.1
15	3.007	0.295 (9.8%)	2.400 (79.8%)	0.312 (10.4%)	10.3 ± 0.8
20	3.000	0.426 (14.2%)	2.574 (85.8%)	-	16.1 ± 1.4

Supplementary Table 4. Product compositions and H₂ consumption data used in Figure 4 to compare catalysts in hydrogenolysis of PE at 300 °C under H₂ (0.992 MPa).

Catalyst	Time (h)	PE (g)	Volatiles g (%)	Liquids g (%)	Solid residue g (%)	H ₂ consumption (mmol)
mSiO ₂	24	3.006	0.078 (2.6%)	0.028 (0.9%)	2.900 (96.5%)	n.a. ^a
ZrO ₂ -30	6	3.001	0.020 (0.7%)	0.378 (12.6%)	2.603 (86.7%)	2.0 ± 0.2
ZrO ₂ -30	12	3.003	0.098 (3.3%)	0.832 (27.7%)	2.073 (69.0%)	3.2 ± 0.5
imp-ZrO ₂ /mSiO ₂	6	3.003	0.077 (2.6%)	0.603 (20.1%)	2.323 (77.4%)	3.1 ± 0.4
ZrO ₂ -6/mSiO ₂	6	3.001	0.020 (0.7%)	0.378 (12.6%)	2.603 (86.7%)	1.9 ± 0.2
ZrO ₂ -6/mSiO ₂	15	3.003	0.412 (13.7%)	0.754 (25.1%)	1.832 (61.0%)	3.6 ± 0.5
Pt/C	6	3.014	0.067 (2.2%)	0.668 (22.2%)	2.279 (75.6%)	5.9 ± 1.1
L-Pt/mSiO ₂	6	3.003	0.079 (2.6%)	1.546 (51.5%)	1.378 (45.9%)	6.7 ± 0.3

^a Not applicable

Supplementary Table 5. Composition of products obtained from the hydrogenolysis of hydrocarbons catalyzed by L-ZrO₂@mSiO₂ under H₂ (0.992 MPa) at 300 °C for 6 h.

Polymer	Reactant g	Volatiles g (%)	Liquids g (%)	Residue g (%)	H₂ consumption mmol	Mass Activity mol H₂·g_{Zr}⁻¹·h⁻¹
n-C ₃₆ H ₇₄	2.994	0.050 (1.7%)	2.944	n.a. ^a	3.5 ± 0.7	2.3 ± 0.5
LDPE <i>M_n</i> = 2.8 kDa <i>M_w</i> = 5.3 kDa	3.003	0.134 (4.5%)	1.422 (47.4%)	1.447 (48.3%)	4.2 ± 0.6	2.7 ± 0.4
LDPE <i>M_n</i> = 20 kDa <i>M_w</i> = 91 kDa	3.003	0.082 (2.7%)	1.257 (42.3%)	1.664 (55.4%)	3.6 ± 0.5	2.3 ± 0.3
Grocery Bag <i>M_n</i> = 10.6 kDa <i>M_w</i> = 150 kDa	2.934	0.049 (1.7%)	1.205 (41.1%)	1.68 (57.3%)	3.6 ± 0.6	2.3 ± 0.4
UHMW PE	3.006	0.086 (2.9%)	1.402 (46.6%)	1.518 (50.5%)	4.1 ± 0.3	2.7 ± 0.1

^a not applicable.

Supplementary Table 6. Total cuts calculated by lumping all molecular weights of gas-liquid and solid phases.

Catalyst	Reaction Time (h)	Total Cuts ^a (mmol)	H ₂ Consumption ^b (mmol)	Mass Activity mol H ₂ ·g _{Metal} ⁻¹ ·h ⁻¹
L-ZrO ₂ @mSiO ₂	2	3.82	1.8 ± 0.2	3.4 ± 0.3
L-ZrO ₂ @mSiO ₂	4	6.27	3.1 ± 0.6	3.0 ± 0.1
L-ZrO ₂ @mSiO ₂	6	8.14	3.6 ± 0.6	2.3 ± 0.1
L-ZrO ₂ @mSiO ₂	8	11.2	5.2 ± 0.7	2.6 ± 0.3
L-ZrO ₂ @mSiO ₂	12	11.4	8.1 ± 1.1	2.6 ± 0.3
L-ZrO ₂ @mSiO ₂	15	17.4	10.3 ± 0.8	2.7 ± 0.3
L-ZrO ₂ @mSiO ₂	20	21.2	16.1 ± 1.4	3.1 ± 0.3
ZrO ₂ -30	6	2.96	2.0 ± 0.2	0.1 ± 0.01
ZrO ₂ -30	12	n.a.	3.2 ± 0.5	0.1 ± 0.02
imp-ZrO ₂ /mSiO ₂	6	3.87	3.1 ± 0.4	2.5 ± 0.5
ZrO ₂ -6/mSiO ₂	6	2.24	1.9 ± 0.2	1.0 ± 0.1
ZrO ₂ -6/mSiO ₂	15	12.6	3.6 ± 0.5	1.0 ± 0.2
Pt/C	6	6.49	5.9 ± 1.1	2.2 ± 0.1
L-Pt/mSiO ₂	6	7.13	6.7 ± 0.3	5.6 ± 1

^a Total Cuts are calculated from the Mn of the entire population of hydrocarbon species, according to eq 3 in the Methods section of the main text. ^b H₂ consumption correlates directly with C-C bonds cleaved. This data and Total Cuts are given for comparison of the analytical methods.

Supplementary Table 7. GPC analysis of polymeric solid residue obtained after catalytic hydrogenolysis and extraction of small molecules with methylene chloride at 100 °C.

Catalyst	Reaction time (h)	M_n (Da)	M_w (Da)	$\bar{D}$
No catalyst: PE starting material	0	20000	96000	4.8
L-ZrO ₂ @mSiO ₂	2	3050	6900	2.3
L-ZrO ₂ @mSiO ₂	4	1990	3800	1.9
L-ZrO ₂ @mSiO ₂	6	1880	3300	1.8
L-ZrO ₂ @mSiO ₂	8	1600	2700	1.7
L-ZrO ₂ @mSiO ₂	12	930	1800	1.9
L-ZrO ₂ @mSiO ₂	15	1100	1990	1.8
imp-ZrO ₂ /mSiO ₂	6	3000	8700	2.9
ZrO ₂ -6/mSiO ₂	6	4500	29600	6.6
ZrO ₂ -6/mSiO ₂	15	1700	5800	3.4
ZrO ₂ -30/mSiO ₂	6	3000	6000	2.0
Pt/C	6	1400	1900	1.4
L-Pt@mSiO ₂	6	2400	3800	1.6

Supplementary Table 8. Ethylene hydrogenation conversion catalyzed by L-ZrO₂@mSiO₂ and pure mSiO₂ platelets with the gas flow rates: He: 13.2 mL/min; H₂: 12.0 mL/min; C₂H₄: 1.20 mL/min at the ambient pressure and 200, 250, and 300 °C.

Temperature (°C)	Conversion (%)	
	L-ZrO ₂ @mSiO ₂	Pure mSiO ₂ platelets
200	12.6	0.1
250	9.9	0.1
300	3.4	0.1

Supplementary Table 9. Gibbs free energies calculated for possible structures of ZrO_xH_y supported on (-111) m-ZrO₂ with reference to the energies of Zr/m-ZrO₂ and gas phase H₂ and H₂O (T = 300 °C; P_{H₂} = 0.90 MPa; P_{H₂O} = 6.89×10⁻¹⁵ MPa). For each ZrO_xH_y (x=0-4; y=0-4) state, we report here only the most stable structure identified from our calculations.

ZrO _x H _y	ΔG (300°C) [eV]	
	PBE-D3	HSE06 ^a
ZrH	-1.02	
Zr(H) ₂	-1.94	
Zr(H) ₃	-2.60	
Zr(H) ₄	-2.58	
ZrO	-2.02	
Zr(O)(H)	-2.81	
Zr(O)(H) ₂	-3.36	-3.64
Zr(OH)(H) ₂	-2.68	
Zr(OH)(H) ₃	-2.53	
Zr(O) ₂	-3.41	-3.84
Zr(O)(OH)	-2.57	
Zr(O)(OH)(H)	-3.34	-3.61
Zr(OH) ₂ (H)	-2.52	
Zr(OH) ₂ (H) ₂	-2.45	-2.60
Zr(O) ₂ (OH)	-1.37	
Zr(O)(OH) ₂	-3.29	-3.62
Zr(OH) ₃	-2.10	
Zr(OH) ₃ (H)	-2.31	-2.44
Zr(O) ₂ (OH) ₂	1.88	
Zr(O)(OH) ₃	-0.06	
Zr(OH) ₄	-2.07	-2.15

^aSingle point energies calculated for the lowest energy structures optimized with PBE-D3 functional.

Supplementary Table 10. Gibbs free energies of reaction (ΔG_{rxn}) and activation (G_a) calculated at a temperature of 300 °C ($P_{\text{gas}} = 0.1$ mPa) for all the elementary steps of n-hexane hydrogenolysis over the $\text{Zr}(\text{O})_2/\text{m-ZrO}_2$ and $\text{H-Zr}(\text{O})\text{OH}/\text{m-ZrO}_2$ models described as $^*\text{Zr}-(\text{O}-\text{O})$ and $\text{H}_{\text{Zr}}-(\text{OH}-\text{O})$, respectively.

ID	Reaction	G_a (T,P ₀) [eV]	ΔG_{rxn} (T,P ₀) [eV]
r ₁	$^*\text{Zr}-(\text{O}-\text{O}) + \text{H}_2(\text{g}) \rightarrow \text{H}_{\text{Zr}}-(\text{OH}-\text{O})$	-	0.08
r ₂	$^*\text{Zr}-(\text{O}-\text{O}) + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{g}) \rightarrow$ $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{O}-\text{O})$	-	0.16
r ₃	$\text{H}_{\text{Zr}}-(\text{OH}-\text{O}) + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3(\text{g}) \rightarrow$ $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)(\text{H})_{\text{Zr}}-(\text{OH}-\text{O})$	-	0.15
r ₄	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{O}-\text{O}) \rightarrow$ $(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{OH}-\text{O})$	1.28	0.40
r ₅	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)(\text{H})_{\text{Zr}}-(\text{OH}-\text{O}) \rightarrow$ $(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)(\text{H}_2)_{\text{Zr}}-(\text{OH}-\text{O})$	1.78	0.68
r ₆	$(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{OH}-\text{O}) \rightarrow$ $(\text{cis-CH}_3\text{CHCHCH}_2\text{CH}_2\text{CH}_3)(\text{H})_{\text{Zr}}-(\text{OH}-\text{O})$	0.94	0.32
r ₇	$(\text{cis-CH}_3\text{CHCHCH}_2\text{CH}_2\text{CH}_3)(\text{H})_{\text{Zr}}-(\text{OH}-\text{O}) \rightarrow$ $^*\text{Zr}-(\text{O}-\text{O}) + \text{cis-CH}_3\text{CHCHCH}_2\text{CH}_2\text{CH}_3(\text{g}) + \text{H}_2(\text{g})$	-	-0.22
r ₈	$(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{OH}-\text{O}) \rightarrow$ $(\text{CH}_3\text{CHCH}_2)(\text{CH}_2\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{OH}-\text{O})$	1.26	0.21
r ₉	$(\text{CH}_3\text{CHCH}_2)(\text{CH}_2\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{OH}-\text{O}) \rightarrow$ $(\text{CH}_2\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{OH}-\text{O}) + \text{CH}_3\text{CHCH}_2(\text{g})$		-0.55
r ₁₀	$(\text{CH}_2\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{OH}-\text{O}) \rightarrow (\text{CH}_3\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{O}-\text{O})$	0.85	-0.09
r ₁₁	$(\text{CH}_3\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{O}-\text{O}) + \text{CH}_3\text{CHCH}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow$ $(\text{CH}_3\text{CHCH}_2)(\text{H})_{\text{Zr}}-(\text{OH}-\text{O}) + \text{CH}_3\text{CH}_2\text{CH}_3(\text{g})$	-	0.33
r ₁₂	$(\text{CH}_3\text{CHCH}_2)(\text{H})_{\text{Zr}}-(\text{OH}-\text{O}) \rightarrow (\text{CH}_3\text{CH}_2\text{CH}_2)_{\text{Zr}}-(\text{OH}-\text{O})$	0.59	-0.80
r ₁₃	$(\text{CH}_3\text{CH}_2\text{CH}_3)_{\text{Zr}}-(\text{O}-\text{O}) \rightarrow ^*\text{Zr}-(\text{O}-\text{O}) + \text{CH}_3\text{CH}_2\text{CH}_3(\text{g})$	-	-0.19

Supplementary References

- 1 Wang, Z.-M., Wang, W., Coombs, N., Soheilnia, N. & Ozin, G. A. Graphene Oxide–Periodic Mesoporous Silica Sandwich Nanocomposites with Vertically Oriented Channels. *ACS Nano* **4**, 7437-7450 (2010).
- 2 Zagdoun, A., Casano, G., Ouari, O., Schwarzwälder, M., Rossini, A. J., Aussenac, F. *et al.* Large Molecular Weight Nitroxide Biradicals Providing Efficient Dynamic Nuclear Polarization at Temperatures up to 200 K. *J. Am. Chem. Soc.* **135**, 12790-12797 (2013).
- 3 Perras, F. A., Boteju, K. C., Slowing, I. I., Sadow, A. D. & Pruski, M. Direct ^{17}O Dynamic Nuclear Polarization of Single-Site Heterogeneous Catalysts. *Chem. Commun.* **54**, 3472-3475 (2018).
- 4 Michaelis, V. K., Corzilius, B., Smith, A. A. & Griffin, R. G. Dynamic Nuclear Polarization of ^{17}O : Direct Polarization. *J. Phys. Chem. B* **117**, 14894-14906 (2013).
- 5 Zhao, X., Hoffbauer, W., Schmedt auf der Günne, J. & Levitt, M. H. Heteronuclear Polarization Transfer by Symmetry-Based Recoupling Sequences in Solid-State NMR. *Solid State Nucl. Magn. Reson.* **26**, 57-64 (2004).
- 6 van Beek, J. D., Dupree, R. & Levitt, M. H. Symmetry-Based Recoupling of ^{17}O – ^1H Spin Pairs in Magic-Angle Spinning NMR. *J. Magn. Reson.* **179**, 38-48 (2006).
- 7 Perras, F. A., Kobayashi, T. & Pruski, M. Natural Abundance ^{17}O DNP Two-Dimensional and Surface-Enhanced NMR Spectroscopy. *J. Am. Chem. Soc.* **137**, 8336-8339 (2015).
- 8 Carravetta, M., Edén, M., Zhao, X., Brinkmann, A. & Levitt, M. H. Symmetry Principles for the Design of Radiofrequency Pulse Sequences in the Nuclear Magnetic Resonance of Rotating Solids. *Chem. Phys. Lett.* **321**, 205-215 (2000).