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Supplementary information

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Stable single-site organonickel catalyst preferentially hydrogenolyses branched polyolefin C–C bonds

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1. Materials and Methods

All procedures for air- and moisture-sensitive compounds were carried out with rigorous exclusion of O_2 and moisture in flame- or oven-dried Schlenk-type glassware interfaced to a high-vacuum ($\sim 10^{-6}$ Torr) line or in an argon-filled M-Braun glovebox with a high-capacity recirculation (<1 ppm O_2). Argon used on high-vacuum lines (Airgas, UHP-grade) was purified by passage through 1MnO/vermiculite and activated Davidson 4A molecular sieve columns. All solvents were dispensed through activated alumina/CuO columns prior to use. The solvent *n*-pentane (Sigma) was further purified by drying over Na/K alloy followed by passage through a fiberglass filter in an argon glovebox. Aluminum oxide was purchased from US Research Nanomaterials, Inc. (gamma, nanopowder **5** nm). Sulfuric acid (98%) was purchased from Fisher. Oxygen (UHP grade) used for calcination was purchased from Airgas and used without further purification. Deuterium (Sigma) and hydrogen (Airgas, UHP) were purified by passage through an oxygen/moisture trap (Matheson, model MTRP-0042-XX). Bis(1,5-cyclooctadiene) nickel (0) was purchased from Sigma-Aldrich and used without further purification. Silica, γ-alumina, polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE), and isotactic polypropylene (*i*-PP) were purchased from Sigma-Aldrich. Silica was calcined at 700 °C for 4 h under O_2 flow and dried under high vac at 500 °C for 1 h. γ–Alumina was calcined at 550 °C for 3 h under O_2 flow and dried under high vac at 450 °C for 1 h. Sulfated alumina (AlS) was synthesized according to previous literature.[1] Polyethylene-co-1-octene (PECO) was kindly provided by Dow Chemical Company. HDPE water bottle caps were from disposable PET water bottles, and water cups were from disposable i-PP water cups. Post-consumer HDPE and i-PP were cut into cm-size pieces and then pumped into the glove box inlet chamber overnight before use.

2. Physical and Analytical Measurements

Inductively coupled plasma (ICP) analysis was conducted at the Northwestern University Quantitative Bio-element Imaging Center. Elemental analyses were performed by Midwest Microlab, Inc. (Indianapolis, IN). A Thermo Scientific ESCALAB 250Xi instrument was used to perform X-ray photoelectron spectroscopy (XPS). An electron flood gun was applied prior to analysis. Peak fitting was performed using Thermo Advantage software, with oxygen (530.8 eV) from support as the binding energy reference. The Ni2p XPS spectrum of commercial $Ni(COD)_2$ was collected as a reference (Figure 3). The samples were loaded onto copper tapes affixed to the

sample holder within a portable chamber inside an Ar-filled glove box. The probe system enabled the samples to be transported from the portable chamber to the spectrometer without exposure to air. The selected spot of air-exposed catalyst **1** was subjected to continuous scanning to determine whether beam-induced reduction occurred during the XPS measurement. The atomic ratios of the two distinct species across different scans are summarized in Table 1.

EPR measurements were performed at X-band (~9.5 GHz) using a Bruker Elexsys E580-X EPR spectrometer outfitted with a Bruker Bruker ER4118X-MS5 resonator. The temperature was maintained at 85 K using an Oxford Instruments CF935 continuous-flow cryostat using liquid nitrogen. The continuous-wave EPR spectra were collected using non-saturating microwave power (~0.8 mW) with 1 mT field modulation at 100 kHz, a 1.28 ms time constant and 5.12 ms conversion time. Spin quantitation was performed by comparing the intensity of the double integral of the spectrum of 12.0 mg AlS/Ni(COD)$_2$ (1.49 μmol Ni) sample to known concentrations of Cu(acac)$_2$ in CH_2Cl_2. Three Cu samples (80 μL) were prepared at concentrations of 0.030 M (2.4 μmol Cu), 0.015 M (1.2 μmol Cu) and 0.0075 M (0.60 μmol Cu); and each spectrum was run twice, reloading the spectrometer and turning each time. Fitting the average of these three concentrations provides a linear calibration curve (y = 3357.5x, Figure 6) from which the spin concentration of AlS/Ni(COD)$_2$ can be estimated to be 0.21 μmol (Table 2), providing a yield of 14%.

Ni K edge XAS was conducted at the Brookhaven National Laboratory (BNL) National Synchrotron Light Source II (NSLS-II) 8-ID ISS beamline. The air-sensitive samples were ground into a fine powder and then pressed as wafers in the glove box, which was loaded into the sample holder sealed with Kapton tape. The AlS/NiH sample was also exposed to air at room temperature by removing Kapton tape for 15 min before measurement. For the spent catalyst sample, it was prepared under ambient conditions. Two ion chambers with a Ni foil in between were placed behind the sample to calibrate the energy. WinXAS was used to fit the first shell peaks in the k^2 weighted Fourier transform of the EXAS data from k = 2.6-10.8 $Å^{-1}$. Ni foil with 12 Ni-Ni bonds at 2.49 Å was fit to determine So, which was 0.80. Optimization of sigma-squared data was obtained from fitting the isolate peaks in k-space.

For scanning transmission electron microscopy (S/TEM), the catalysts were dispersed in methanol and drop-cast onto ultrathin carbon-coated Cu grids. A JEOL ARM 200F S/TEMequipped with a cold field emission gun (FEG) and dual Silicon Drift Detectors (SDDs) energy dispersive

spectroscopy (EDS) detectors (1.7 sr) was used for high-angle annular dark-field (HAADF) imaging and EDS analysis. The analysis was implemented at 200 kV accelerating voltage with an emission current of 15 μA.

^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra of the hydrogenolysis products were obtained with a Bruker Avance III system equipped with a DCH Cryoprobe. Solid-state NMR experiments were performed on a 9.4 T Bruker Biospin Avance III spectrometer, equipped with a 3.2 mm triple resonance probe. The sample was packed in the sapphire MAS rotor in an Ar-filled glove box and spin at 10 kHz using nitrogen gas, to minimize contamination from atmospheric moisture. $^{13}C\{^{1}H\}$ cross-polarization magic-angle spinning (CPMAS) spectra were obtained at 110 K, using a CP contact time of 500 μs.

Continuous flow catalytic experiments using propane and iso-butane as model complexes were carried out on an Altamira BenchCAT™ 4000R HP plug-flow reactor. The catalyst was diluted with quartz sand in a 1/10 ratio (m/m). This mixture was contained in a 9 mm I.D. quartz tube. An Agilent 6850 gas chromatograph equipped with an HP-PLOT Q column was used to separate hydrocarbon products in the effluent gas. The GC oven was held at a constant 150 °C with a 4.932 mL/min flow rate. Chromatographic data were recorded for 6 min per injection for propane and 9 min per injection for isobutane. An FID detector was used for quantitation of hydrocarbons. In a typical experiment, in the glove box, 60 mg of AlS/Ni$(COD)_2$ precatalyst was mixed with 600 mg quartz sand. The mixture was loaded into the reactor tube, sealed, removed from the glove box, then connected to the reactor system. Before opening the reactor to the gas manifold, the upstream portion of the manifold was purged with argon for at least 10 min (50 sccm). Before flowing alkane/H_2 mixture, H_2 was passed over the catalyst bed at 10 sccm for a minimum of 60 min at 150 °C. Reactions were carried out at 2 atm total pressure. Effluent gas was sampled at intervals of 7.5 min for propane and 10 min for isobutane substrates, respectively. Reaction conversion was measured as a function of propane or iso-butane consumption.

Gas chromatography-mass spectrometry (GC-MS) analysis of hydrogenolysis product mixtures was carried out on an Agilent GCMSD equipped with a DB5 column (oven program: **1.** 2 min. 50 °C hold **2.** 30 °C / min ramp **3.** 5 min hold at 300 °C). Split mode injection at 2 μL / injection and a 100:1 split ratio was used. Gel permeation chromatography analysis (GPC) was carried out on a Polymer Char instrument equipped with an IR spectrometer. The solvent 1,2,4-trichlorobenzene

was used to dissolve the polymer sample and used as an eluent. Diffuse reflectance infrared spectroscopy (DRIFTS) measurements were obtained on a Thermo 6700 infrared spectrometer equipped with a Harrick Praying Mantis DRIFTS attachment. KBr windows were used for the DRIFTS cell. Anhydrous KBr was used as a background. The DRIFTS cell contained dry glovebox Ar (<1 ppm O_2 / <1 ppm H_2O) during all measurements.

DFT-based simulations were performed with the Quickstep package, using a hybrid Gaussian and plane wave method.[2] A double quality DZVP Gaussian basis set was employed for the Al and Ni atoms, and a triple quality TZVP Gaussian basis set was employed for all the other atoms. The Goedecker-Teter-Hutter pseudopotentials[3] together with a 400 Ry plane wave cutoff were used to expand the densities obtained with the Perdew-Burke-Ernzerhof (PBE)[4] exchange-correlation density functional, and vdW forces are taken in account with the Grimme D3 Method.[5] Only the gamma point was considered in a supercell approach. Periodic boundary conditions are applied in all directions of space. Molecular graphics[3] were produced by the CHEMCRAFT graphical package.[6] Gibbs free energy profile: enthalpic and entropic contributions along the reaction pathway were evaluated by performing the frequency calculation of the corresponding molecular species at 298.15 K and 1 atm using the ORCA software package (version 4.1.0). In this context, adsorbed catalysts were modeled by simple molecular species (MeONiH). ORCA calculations were performed at the level of the B3LYP-D3/ ZORA-def2-TZVP. The relativistic effective core potential of Ni was described with ZORA.[7] The enthalpic and entropic contributions were then "appended" to the SCF energy profile to obtain the Gibbs free energy profile.

3. AlS Synthesis

Under atmospheric conditions, sulfuric acid (2.0 M aqueous solution prepared from deionized (DI) water, 288 mL) was added to 7.0 g of aluminum oxide with stirring. The suspension was stirred for 30 min, then centrifuged (4000 rpm/3390 g, 5 min). The supernatant was discarded, and the alumina was re-suspended in DI water and centrifuged; this step was repeated until a pH of ~6 was achieved (typically 7 washings in total). The resulting solids were dried at 120 °C and ~10^{-6} Torr for 18 h. The solids were then crushed *via* mortar and pestle and sieved to 180 mesh (80 μm). The powder was loaded into a quartz boat, placed in a tube furnace, and calcined at 550 °C under flowing O_2 (~2 L/min) for 3 h. The reaction tube was then interfaced to the high vacuum line and pumped down to ~10^{-6} Torr for 1 h at 450 °C. The furnace was next cooled under vacuum, and the

closed reaction tube was brought into an argon glovebox. The **AlS** (white powder, 4.83 g) was recovered and stored in a sealed container under argon.

4. Chemisorption of Ni(COD)$_2$ on AlS

In a dry two-sided fritted reaction vessel, 20 mL of pentane was condensed onto well-mixed quantities of Ni(COD)$_2$ (162 mg, 0.589 mmol) and **AlS** (4.05 g). The resulting slurry was stirred at 25 °C for 2 h, and then filtered. After chemisorption, the solid attained a light brick red color. The impregnated support was collected on the frit and washed five times with ~5 mL portions of pentane and then dried in vacuo for 1 h. ^{1}H NMR was used to check for presence of remaining physiosorbed (weakly bound) Ni(COD)$_2$ by addition of ~10 mg of solids directly to an NMR tube with benzene-d_6 or toluene-d_8 used as the solvent. If residual organometallic was present, the catalyst was additionally washed with pentane as described above until Ni(COD)$_2$ was no longer visible in the ^{1}H NMR. The catalyst was then stored in a sealed container at -40 °C in an argon glovebox until needed for use. The catalyst **AlS/Ni(COD)$_2$** loading was determined to be 0.73 wt. % Ni (0.13 mmol/g catalyst, the average of ICP-OES analysis from 3 different batches of catalysts: 0.75 wt%, 0.72 wt%, and 0.71 wt%, respectively) by ICP-OES. Elem. Anal. Calcd for **1**: C, 2.50%; H, 0.31%. Found: C, 2.48% (2.06 mmol/g catalyst); H, 0.53% (5.30 mmol/g catalyst). EPR analysis: s = ½; g = 2.0339, 2.0308, and 2.509.

5. Chemisorption of Ni(COD)$_2$ on alumina

In a two-sided fritted dried reaction vessel, 20 mL of pentane was condensed onto well-mixed quantities of Ni(COD)$_2$ (62 mg, 0.223 mmol) and alumina (1.51 g). The resulting slurry was stirred at 25 °C for 2 h, and then filtered. After chemisorption, the solid attained a light brick red color. The impregnated support was collected on the frit and washed five times with ~5 mL portions of pentane and then dried in vacuo for 1 h. ^{1}H NMR was used to check for the presence of remaining physiosorbed (weakly bound) Ni(COD)$_2$ by the addition of ~10 mg of solids directly to an NMR tube with benzene-d_6 or toluene-d_8 used as the solvent. If residual organometallic was present, the catalyst was additionally washed with pentane as described above until Ni(COD)$_2$ was not visible in the ^{1}H NMR. The catalyst was then stored in a sealed container at -40 °C in an argon glovebox until needed for use. The catalyst **Al$_2$O$_3$/Ni(COD)$_2$** loading was determined to be 0.70 wt. % Ni (0.12 mmol/g catalyst) by ICP-OES.

6. Chemisorption of Ni(COD)$_2$ on silica

In a two-sided fritted dried reaction vessel, 20 mL of pentane was condensed onto well-mixed quantities of **Ni(COD)$_2$** (22 mg, 0.080 mmol) and **silica** (514 mg). The resulting slurry was stirred at 25 °C for 2 h, and then filtered. After chemisorption, the solid attained a light brick red color. The impregnated support was collected on the frit and washed five times with ~5 mL portions of pentane and then dried in vacuo for 1 h. ^{1}H NMR was used to check for presence of remaining physiosorbed (weakly bound) **Ni(COD)$_2$** by addition of ~10 mg of solids directly to an NMR tube with benzene-d_6 or toluene-d_8 used as the solvent. If residual organometallic was present, the catalyst was additionally washed with pentane as described above until **Ni(COD)$_2$** was no longer visible in the ^{1}H NMR. The catalyst was then stored in a sealed container at -40 °C in an argon glovebox until needed for use. The catalyst **SiO$_2$/Ni(COD)$_2$** loading was determined to be 0.34 wt. % Ni (0.06 mmol/g catalyst) by ICP-OES.

7. Synthesis of AlS/NiH

In the glovebox, **AlS/Ni(COD)$_2$** (~400 mg) was placed in a 75 mL glass pressure reactor. The reactor was sealed, interfaced with a high-pressure/high vacuum line, evacuated, and then charged with 2.5 atm H_2. The reactor was heated to 200 °C for 3 h, then evacuated. The catalyst color changed from light brick red to pale grey. This cycle was repeated once more. The solid was then used as needed for further reactions or measurements.

8. Synthesis of AlS/NiD

In the glovebox, **AlS/Ni(COD)$_2$** (~400 mg) was placed in a 75 mL glass pressure reactor. The reactor was sealed, interfaced with a high-pressure/high vacuum line, evacuated, and then charged with 2.5 atm D_2. It was subsequently heated to 200 °C for 3 hours, followed by evacuation. This cycle was repeated once more. The resulting solid was then utilized for further reactions or measurements as needed.

9. Quantification of Ni-H sites: reaction of AlS/NiD with excess PhCH$_2$Cl

Exactly 305 mg of **AlS/NiD** (0.038 mmol Ni) was loaded into a reaction vessel equipped with a quarter-inch sidearm. Then, 12.9 μL dried $PhCH_2Cl$ (0.112 mmol) was added to **AlS/NiD** powder via syringe. The $PhCH_2D$ generated after 16 h of stirring at room temperature was trapped with liquid N_2 under a high vacuum and then was measured with ^{1}H NMR with 6.3 μL 1,4-dioxane

(0.076 mmol) as the internal standard (Figure 7). Quantification based on the internal standard revealed the formation of 0.1 equiv of $PhCH_2D$, presumably due to the incomplete reaction of Ni-D (~300 mg solid) with $PhCH_2Cl$ (12.9 µL liquid).

To ensure a complete reaction of the Ni-D sites, the experiment was repeated at 110 °C with an increased amount of $PhCH_2Cl$ (130 µL, 1.12 mmol). Under these conditions, the reaction was not entirely selective, leading to the formation of both $PhCH_2D$ and C_6H_5D, as observed by ^1H NMR (Figure 8). Quantification based on the internal standard revealed the formation of 0.68 equivalents of C_6H_5D and $PhCH_2D$, indicating that at least 68% of the Ni sites were present as Ni-D.

10. Synthesis of AlS/NiCl

280 mg of **AlS/NiH** (0.035 mmol Ni) was loaded into a reaction vessel. 75 µL dried heptyl chloride (0.35 mmol) was added to **AlS/NiH** powder dropwise via syringe. The resulting mixture was stirred at room temperature for 20 h before drying under high vacuum for 1 h. The resulting solid was then utilized for further reactions or measurements as needed.

11. Ethane hydrogenolysis attempt with AlS/NiH

Exactly 210 mg of **AlS/NiH** (0.038 mmol Ni) was loaded into a heavy-walled glass pressure reactor (150 mL volume) in an Ar-filled glove box. The reactor was sealed with a threaded Teflon cap with an NPT valve installed. The reactor was degassed and refilled with 2 atm H_2/Ethane (1/1 ratio), then placed in a 200 °C oil bath for 20 h. A headspace sample was measured by GC-Fid **(Figure** 29).

12. BentchCat continuous flow experiments

In the glove box, 60 mg of $AlS/Ni(COD)_2$ precatalyst was mixed with 600 mg quartz sand. The mixture was loaded into the the BentchCat reactor tube, and sealed with 3-way valves, removed from the glove box, and then connected to the reactor system. Before opening the reactor to the gas manifold, the upstream portion of the manifold was purged with argon for at least 5 min (50 sccm). The reactor was then heated to 150 °C at a ramp rate of 5 °C/min under a continuous flow of 20 sccm H_2. The temperature was maintained at 150 °C for 60 min before being further increased to 200 °C at the same ramp rate. After holding at 200 °C for 10 min, a gas mixture comprising 10 sccm of 9.9% alkane (propane or isobutane) and 10 sccm of pure H_2 was introduced into the reactor. The reactor temperature was held constant for an additional 24 h. The composition of the

effluent stream was analyzed using GC-FID chromatography, with a runtime of 6 minutes per injection for propane and 9 minutes per injection for isobutane.

13. General Polyolefin Hydrogenolysis Procedure

In the glovebox, **AlS/Ni(COD)$_2$** or regenerated catalyst and the desired amount (~500 mg) of polyolefin (PE, PECO, or PP) were loaded into a 25 mL Parr autoclave reactor with a PTFE liner and magnetically coupled stirring with ~20% mass loading of the catalyst (~100 mg, 0.033 mol% Ni). The Parr reactor was sealed inside the glovebox and then transferred to the Parr heating controller outside of the glovebox. After degassing, the Parr reactor was refilled with 17 atm H_2 at room temperature. The desired temperature was set to 200 °C on the controller. Once the temperature reached 195 °C, stirring was set at 1500 rpm, and the time interval was started. At the end of the time interval, the Parr reactor was removed from the heater and then cooled to room temperature with a strong airflow. If needed, headspace samples were taken at this point. The reactor was vented through the gas release valve and opened to the air. Approx. 5 mL DCM was next used to wash the head of the Parr reactor. These washings were added to the reactor. Solids were suspended in the DCM washings and then filtered to isolate the solids. The reactor was washed multiple times to remove all residue. The solids were washed ~3x with 5 mL portions of DCM, then dried at ~100 mTorr overnight (solid fraction). The DCM was removed from the filtrate (DCM extract fraction), and the resulting liquid was dried overnight at ~100 mTorr. The "volatiles" fraction was calculated by the difference between the initial polyolefin mass and the sum of solid faction and DCM extract fraction. The percent conversion of a polyolefin hydrogenolysis reaction is defined as the mass of "volatiles" and "DCM extract" produced as a percentage of the initial polyolefin mass. This accounting for polyolefin converted into volatiles and liquids is taken to be the mass balance and data are reported in manuscript Tables 1, 2, 3, 4, and 7.

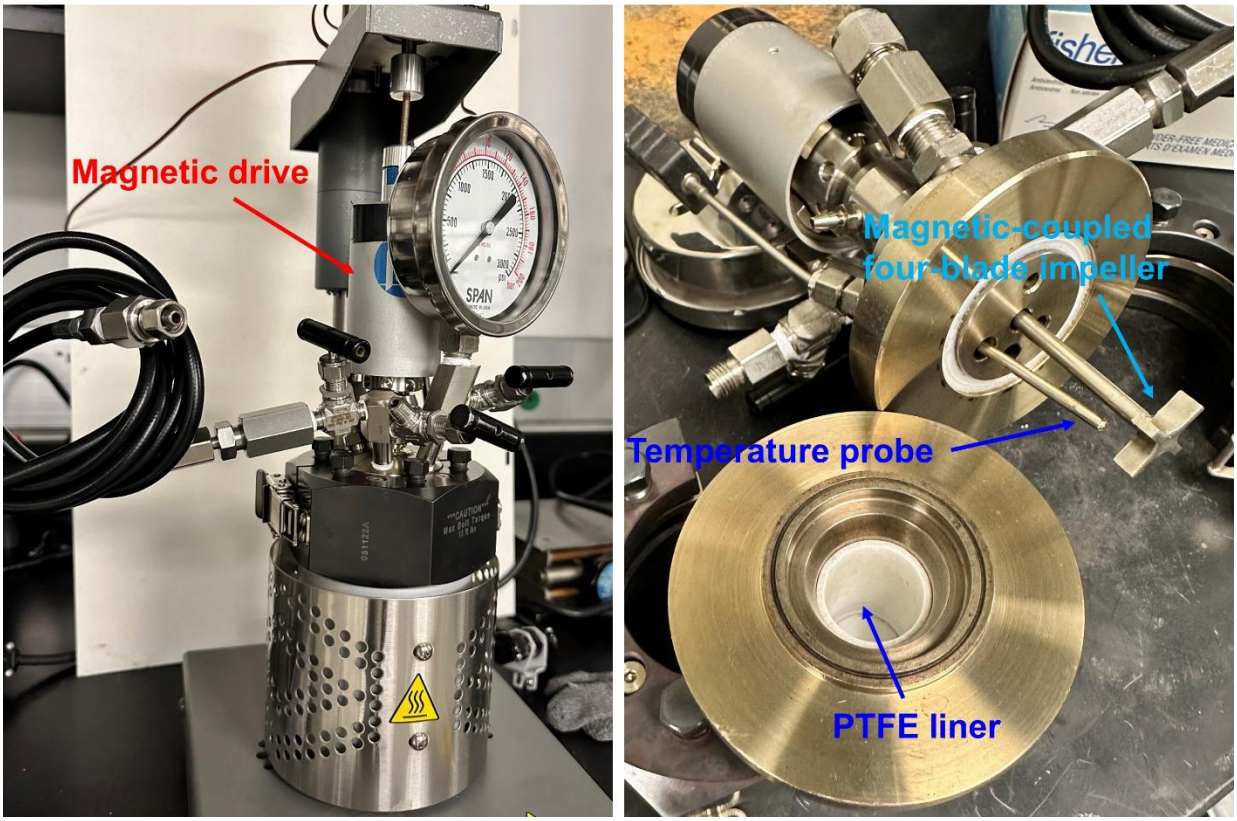

Figure 1. High-pressure compact reactor vessel (Parr reactor) and its parts.

14. General Procedure for Hydrogenolysis of *i*-PP and PVC Mixtures

In the glovebox, **AlS/Ni(COD)$_2$** and the desired amount of *i*-PP and PVC polymer mixtures were loaded into a 25 mL Parr autoclave reactor with a PTFE liner and magnetically coupled stirring with ~20% mass loading of the catalyst (~100 mg, 0.033 mol% Ni). The Parr reactor was sealed inside the glovebox and then transferred to the Parr heating controller outside of the glovebox. After degassing, the Parr reactor was refilled with 17 atm H_2 at room temperature. The desired temperature was set to 200 °C on the controller. Once the temperature reached 195 °C, stirring was set at 1500 rpm, and the time interval was started. At the end of the time interval, the Parr reactor was removed from the heater and then cooled to room temperature with a strong airflow. If needed, headspace samples were taken at this point. The reactor was vented through the gas release valve and opened to the air. Approx. 5 mL DCM was next used to wash the head of the Parr reactor. These washings were added to the reactor. Solids were suspended in the DCM washings and then filtered to isolate the solids. The reactor was washed multiple times to remove all residue. The solids were washed ~3x with 5 mL portions of DCM, then dried at ~100 mTorr overnight (The

unreacted PVC polymer was subtracted when calculating solid fraction). The DCM was removed from the filtrate (DCM extract fraction), and the resulting liquid was dried overnight at ~100 mTorr. The "volatiles" fraction was calculated by the difference between the initial polyolefin mass and the sum of solid faction and DCM extract fraction. The percent conversion of a polyolefin hydrogenolysis reaction is defined as the mass of "volatiles" and "DCM extract" produced as a percentage of the initial polyolefin mass.

15. Procedure for spent AlS/Ni regeneration

The white spent catalyst, recovered from the DCM work-up of *i*-PP hydrogenolysis, was dried at 200 °C under high vacuum for 20 h. The dried catalyst was then transferred to the glovebox, where 10 mL of pentane was added with stirring, followed by the addition of the desired amount of $AlEt_3$ to the resulting suspension. Upon addition, the white catalyst powder immediately turned gray. The mixture was stirred at 25°C for 10 min before all volatiles were removed under high vacuum. The catalyst was further dried for 30 min before being transferred back to the glovebox for storage.

Table 1. XPS**.** Atomic% of air-exposed catalyst at different X-ray beam exposure scan numbers

Entry	Number of scans	Atomic% with BE at 853.8 (Ni^0)	Atomic% with BE at 856.9 (Ni^{II})
1	15	11.2	88.7
2	30	14.3	85.7
3	45	19.7	80.3
4	60	22.4	77.6
5	90	28.6	71.4

Table 2. EPR spin quantification data

Entry	Sample	Intensity of double integral[a]	Errors between 2 measurements	Cu(II) or Ni(I)/μmol
1	0.030 M $Cu(acac)_2$	7864	11.3%	2.4
2	0.015 M $Cu(acac)_2$	4010	1.1%	1.2
3	0.0075 M $Cu(acac)_2$	2828	48.6%	0.60
4	AlS/$Ni(COD)_2$	710	17.9%	0.21

[a]. average integral of two measurements of the same EPR sample.

Table 3. Catalyst screening and control hydrogenolysis experiments with PECO[a]

Entry	Catalyst	mol% Ni	Time (h)	Solid%	DCM Extract%	Volatiles %	Activity[b]
1	AlS/Ni(COD)$_2$	0.035	2	23.4	56.6	20.0	1100
2	AlS/Ni(COD)$_2$	0.034	2	28.7	52.7	18.6	1050
3	AlS/Ni(COD)$_2$	0.031	2	25.5	62.7	11.8	1190
4	AlS/Ni(COD)$_2$	0.033	2	26.2	51.8	22.0	1130
5	AlS/NiH	0.033	2	30.6	57.3	12.1	1050
6	AlS/NiH	0.034	2	28.1	54.1	17.8	1070
7	AlS/NiH	0.034	2	31.3	53.4	15.3	1020
8	AlS (110.3 mg)	0	24	0	0	0	0
9	Ni(COD)$_2$	0.077	4	0	0	0	0
10	Al_2O_3/Ni(COD)$_2$	0.032	8	89.9	9.9	0.2	15
11	Al_2O_3/Ni(COD)$_2$	0.032	24	90.0	7.0	3.0	5
12	SiO_2/Ni(COD)$_2$	0.031	8	95.8	1.4	2.8	10

[a] Reaction conditions: Neat substrate (~500 mg PECO), ~100 mg catalyst (~0.7 mg Ni) or support or 8 mg of Ni(COD)$_2$, 17 atm H_2, 1500 rpm at 200 °C in Parr reactor with 25 mL internal volume [b] units: (mol CH_2 equiv. volatiles + DCM extract)·(mol Ni)$^{-1}$·(h)$^{-1}$

Table 4. GPC analysis of DCM extract of hydrogenolysis of commercial *i*-PP and a-PP

Entry	PP type	Rxn. Time (min)	Mw (g/mol)	Mn (g/mol)	Mw/Mn
1	isotactic	0	28232	9601	2.94
2	isotactic	20	4267	911	4.68
3	isotactic	40	3483	861	4.05
4	isotactic	60	2398	666	3.60

6	isotactic	120	1544	595	2.61
7	atactic	0	35196	6428	5.48
8	atactic	40	7853	874	8.98

Table 5. GPC analysis of hydrogenolysis of post-consumer *i*-PP (bottle cap)

Entry	Rxn. Time (min)	Mw (g/mol)	Mn (g/mol)	Mw/Mn	SCB/1000C[a]
1	0	322392	48378	6.66	356.7
2	40	5813	1938	3.00	350.3
3	60	4428	1375	3.22	346.9

[a]. SCB/1000C: Short-chain branching obtained from GPC-IR analysis based on the ratio of CH_3/CH_2.

Table 6. GPC analysis of step-wise hydrogenolysis of mixtures of *i*-PP (81% water cup) and linear PE (19% bottle cap) for 1 h at 200 ˚C.

Entry	Polymer/product	Mw (g/mol)	Mn (g/mol)	Mw/Mn	SCB/1000C[a]
1	Starting PE	65481	16264	4.03	9.3
2	Starting *i*-PP	322392	48378	6.66	356.7
3	Solid	62478	11212	5.57	17.4
4	DCM extract	3662	1308	2.80	343.1

[a]. SCB/1000C: Short-chain branching obtained from GPC-IR analysis based on the ratio of CH_3/CH_2.

Table 7. GPC analysis of step-wise hydrogenolysis of mixtures of *i*-PP (48% water cup) and linear PE (52% bottle cap) for 1 h at 200 ˚C.

Entry	Polymer/product	Mw (g/mol)	Mn (g/mol)	Mw/Mn	SCB/1000C[a]
1	Starting PE	65481	16264	4.03	9.3
2	Starting *i*-PP	322392	48378	6.66	356.7
3	Solid	47003	5271	8.92	33.5
4	DCM extract	5532	1355	4.08	300.3

[a]. SCB/1000C: Short-chain branching obtained from GPC-IR analysis based on the ratio of CH_3/CH_2.

Table 8. GPC analysis of DCM extract of *i*-PP (Sigma-Aldrich) hydrogenolysis in the presence of PVC (Sigma-Aldrich) with constant total polymer mass (~500 mg) for 40 min at 200 ˚C

Entry	Polymer substrate	Time (min)	Mw (g/mol)	Mn (g/mol)	Mw/Mn
1	*i*-PP	0	322392	48378	6.66
2	*i*-PP	40	3483	861	4.05
3	90% i-PP+10%PVC	40	1133	298	3.80
4	50% i-PP+50%PVC	40	775	281	2.76

Table 9. GPC analysis of DCM extract of *i*-PP (Sigma-Aldrich) hydrogenolysis in the presence of PVC (Sigma-Aldrich) with consistent i-PP loading (~500 mg) for 40 min at 200 ˚C

Entry	Polymer substrate	Time (min)	Mw (g/mol)	Mn (g/mol)	Mw/Mn
1	*i*-PP	0	322392	48378	6.66
2	*i*-PP	40	3483	861	4.05
3	10%PVC	40	3127	398	7.87
4	25%PVC	40	1528	401	3.81

Table 10. GPC analysis of DCM extract of *i*-PP (Sigma-Aldrich) hydrogenolysis under various conditions (e.g., pretreated catalyst or PTFE additive).

Entry	Polymer substrate	Time (min)	Mw (g/mol)	Mn (g/mol)	Mw/Mn
1	*i*-PP	0	322392	48378	6.66

2	*i*-PP	40	3483	861	4.05
3	10% PTFE	40	3918	837	4.68
4	*i*-PP[a]	40	10555	1551	6.80
5	10% PVC[b]	40	6344	942	6.73

[a]. AlS/Ni(COD)$_2$ catalyst pretreated with PVC. [b]. PVC was placed below the reaction vessel.

Table 11. Computed energy values (kcal/mol) associated with the catalytic hydrogenolysis process shown in Figure 6

	ΔE(kcal/mol)	**ΔH(kcal/mol)**	**ΔG(kcal/mol)**
INT1 + Propane	0.0	0.0	0.0
INT2	-27.2	-26.6	-32.0
TS1	-16.2	-18.6	-22.7
INT3	-18.6	-20.1	-25.7
TS2	6.6	3.2	-1.5
INT4	-10.6	-14.5	-21.5
TS3	2.2	-2.3	-6.1
INT5 + Methane	-12.1	-13.9	-16.1
TS4	-9.2	-11.9	-13.1
INT6	-21.1	-20.3	-22.3
INT7 +H2	-36.2	-34.4	-38.7
TS5	-31.4	-30.4	-33.3
INT8	-39.6	-35.1	-39.3
INT2 + Ethane + propane	-43.7	-39.8	-44.1

Table 12. Optimization of AlS/Ni regeneration conditions[a]

Entry	**Catalyst**	**Equiv. $AlEt_3$**	**Catalyst loading**	**PECO (mg)**	**Solid %**	**DCM extract %**	**Volatile %**	**Activity** [b]

1	**1**	-	106.2	533.2	23.4	49.6	27.0	1100
2	Spent	-	104.1	523.0	100	0	0	0
3	Spent	2	101.6	525.9	91.2	7.1	1.7	130
4	Spent	3	99.2	531.9	79.2	12.3	8.6	320
5	Spent	4	104.2	528.9	57.4	34.2	8.4	620
6	Spent	4.5	100.4	534.8	60.7	30.5	8.8	600
7	Spent	5	101.9	543.7	64.1	29.0	6.9	550
8	Spent	6	102.6	534.3	67.9	25.8	6.3	480
9	Spent	20	100.5	522.8	75.7	17.1	7.2	360
10	AlS	4	100.9	501.9	100	0	0	0

[a] Reaction conditions: Neat substrate, ~ 0.03 mol% Ni (~0.7 mg), 17 atm H_2, 1500 rpm at 200 °C for 2 h in Parr reactor with 25 mL internal volume. [b] units: mol CH_2 equiv. (volatiles + DCM extract)·(mol Ni)$^{-1}$·(h)$^{-1}$.

Table 13. Catalytic *i*-PP hydrogenolysis using a recycled catalyst over 4 runs.[a]

Entry	*i*-PP (g)	AlS/Ni (g)	Runs	Time (min)	Solid (mg)	DCM Extraction (g)	Volatiles (mg)	Activity[b]
1	1.5363	0.3091	1st	40	15.0	1.4718	63.0	4270
2	1.2664	0.2465	2nd	40	10.1	1.2284	27.9	4390
3	1.1076	0.2217	3rd	40	10.0	1.0666	31.0	4260
4	0.9836	0.1913	4th	40	7.9	0.9492	26.6	4310

[a] Reaction conditions: Neat substrate, ~0.03 mol% Ni loading, 17 atm H_2, 1500 rpm at 200 °C in Parr reactor with 25 mL internal volume [b] units: (mol CH_2 equiv. volatiles + DCM extract)·(mol Ni)$^{-1}$·(h)$^{-1}$

Table 14. GPC analysis of DCM extract of Catalytic i-PP hydrogenolysis (40 min at 200 °C) using a recycled catalyst over 4 runs.

Entry	Catalyst	Mw (g/mol)	Mn (g/mol)	Mw/Mn
1	AlS/Ni(COD)$_2$	2796	913	3.06
2	1st regeneration	11663	2759	4.23
3	2nd regeneration	12159	2807	4.33

4	3rd regeneration	13544	3046	4.45

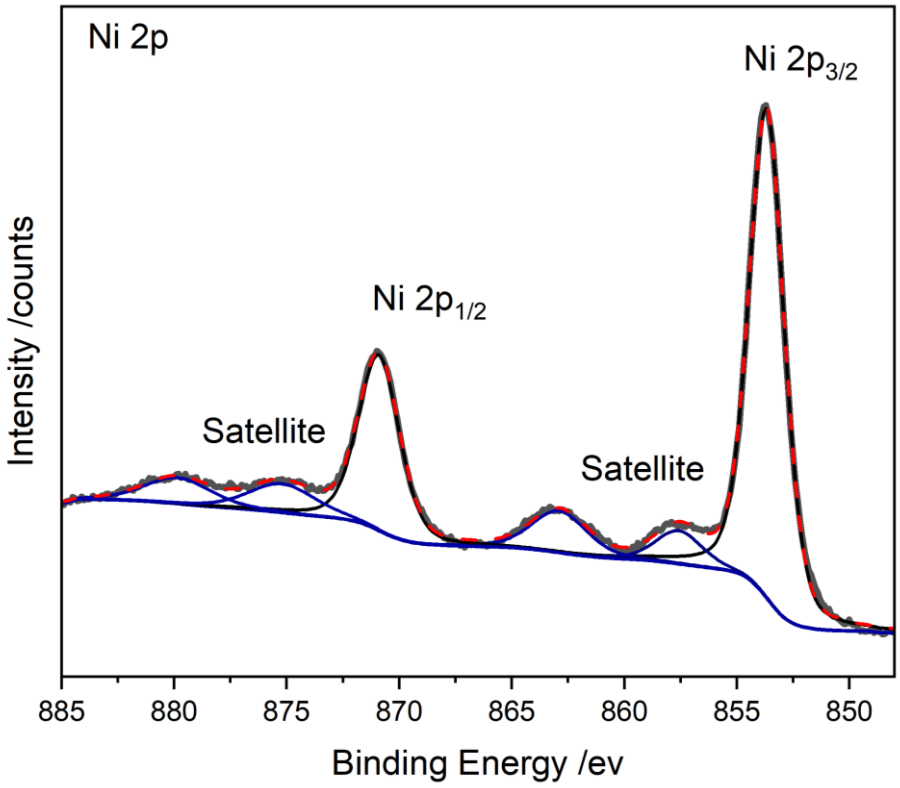

Figure 2. Ni 2P XPS spectrum of $Ni(COD)_2$.

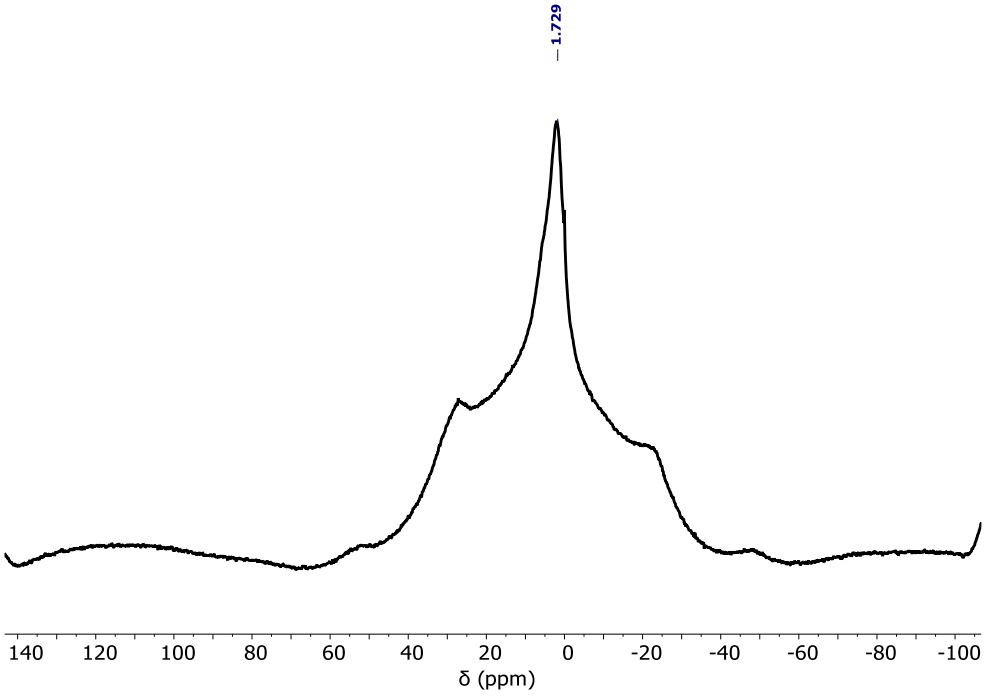

Figure 3. ^{1}H SSNMR spectrum (400 MHz) of Catalyst **1** measured in a 4 mm rotor at 10 kHz spinning rate at room temperature.

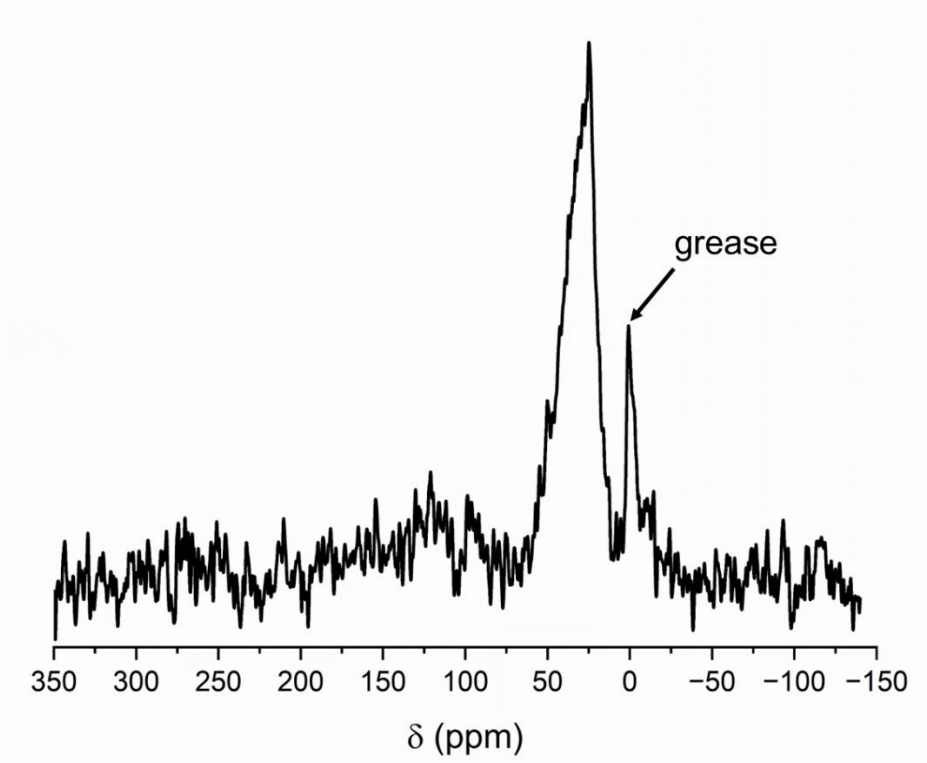

Figure 4. ^{13}C MAS SSNMR spectrum of Catalyst **1** collected at 110 K, using a CP contact time of 500 μs and a spinning rate of **10** kHz

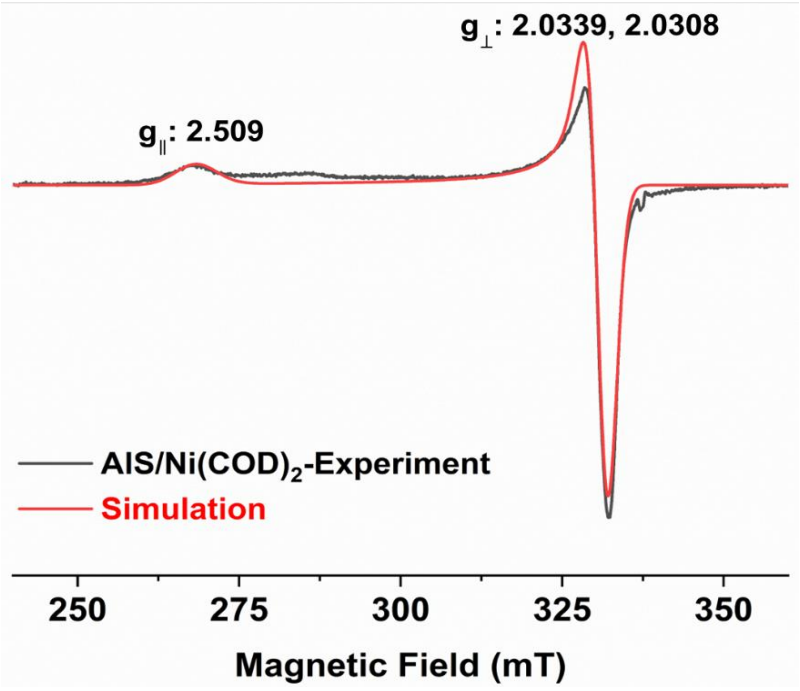

Figure 5. Continuous-wave EPR spectrum of **AlS/Ni(COD)$_2$** at the X-band (9.400 GHz) at 85 K.

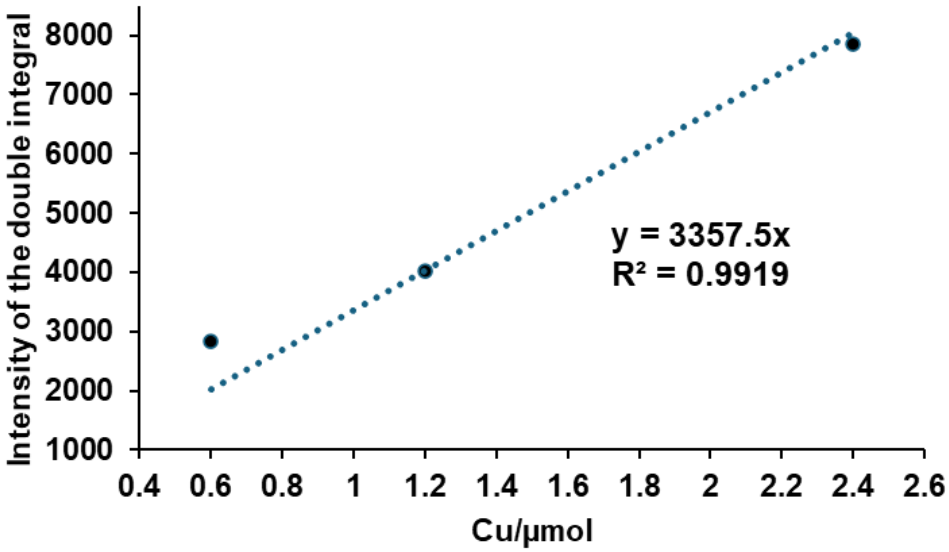

Figure 6. Calibration curve for EPR spin quantification using Cu(acac)$_2$ as a standard.

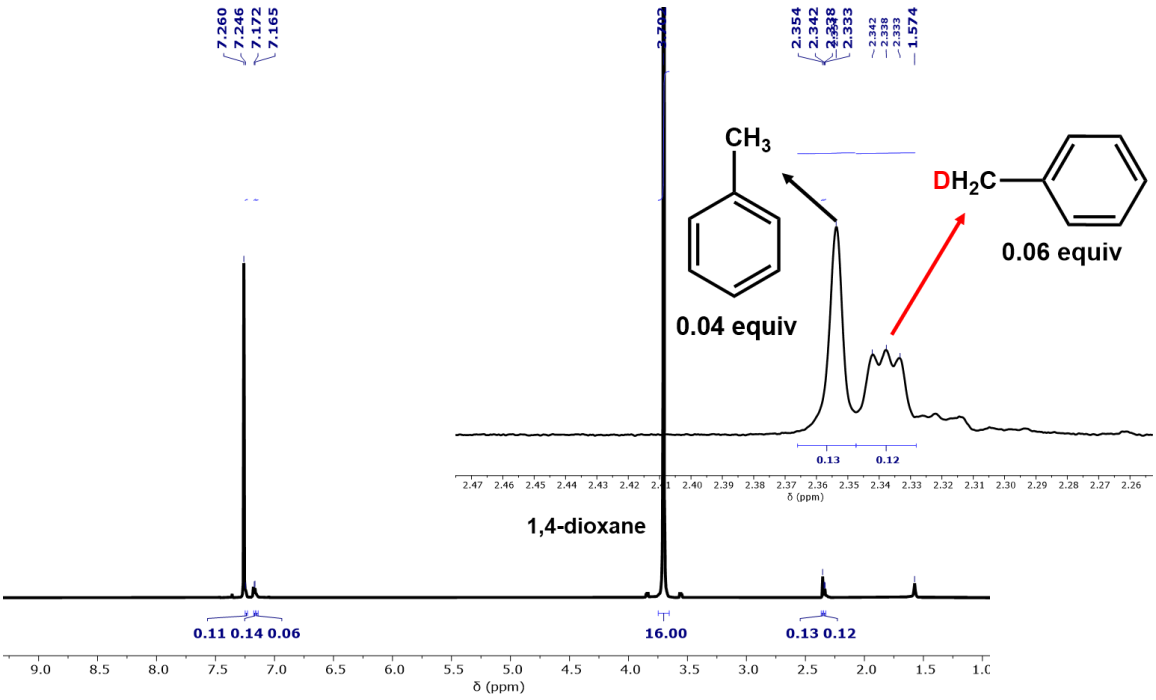

Figure 7. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of the volatile product collected in a liquid N_2 trap in the reaction of AlS/NiD with $PhCH_2Cl$ at room temperature.

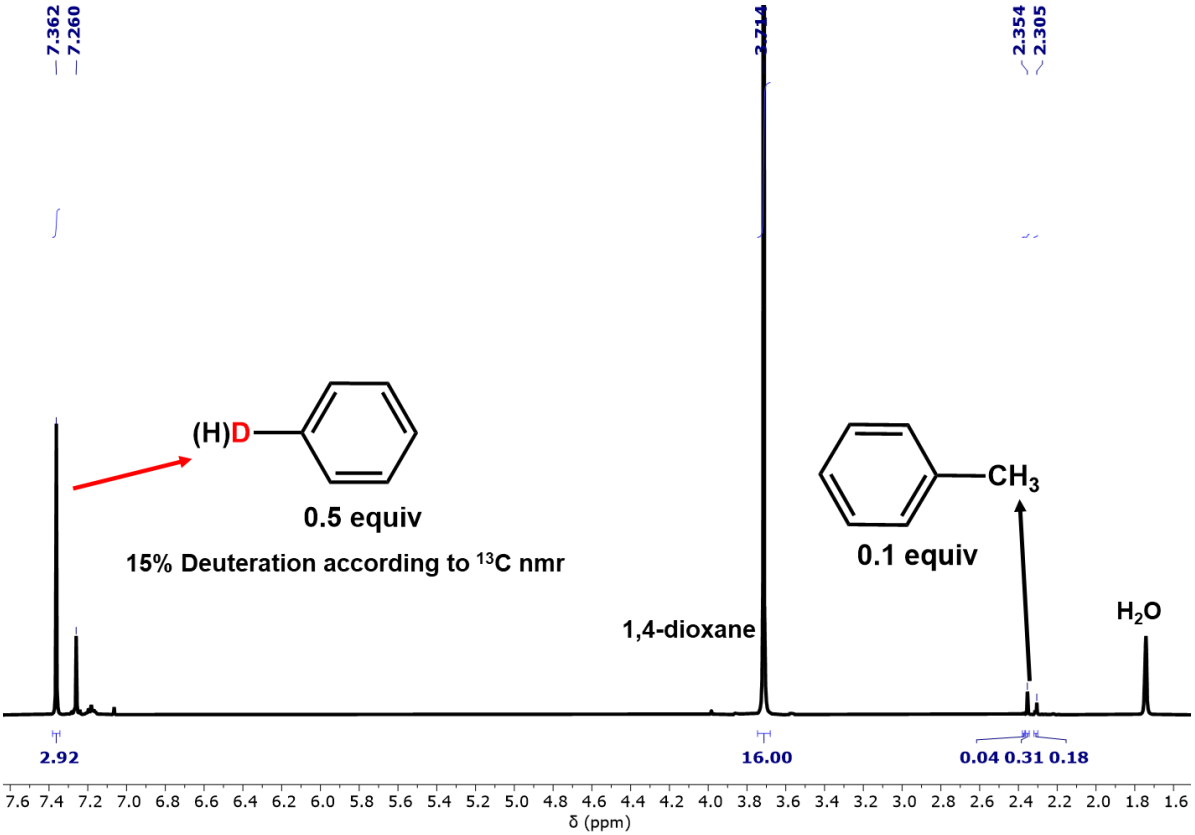

Figure 8. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of the volatile product collected in a liquid N_2 trap in reaction of AlS/NiD with $PhCH_2Cl$ at 110 °C.

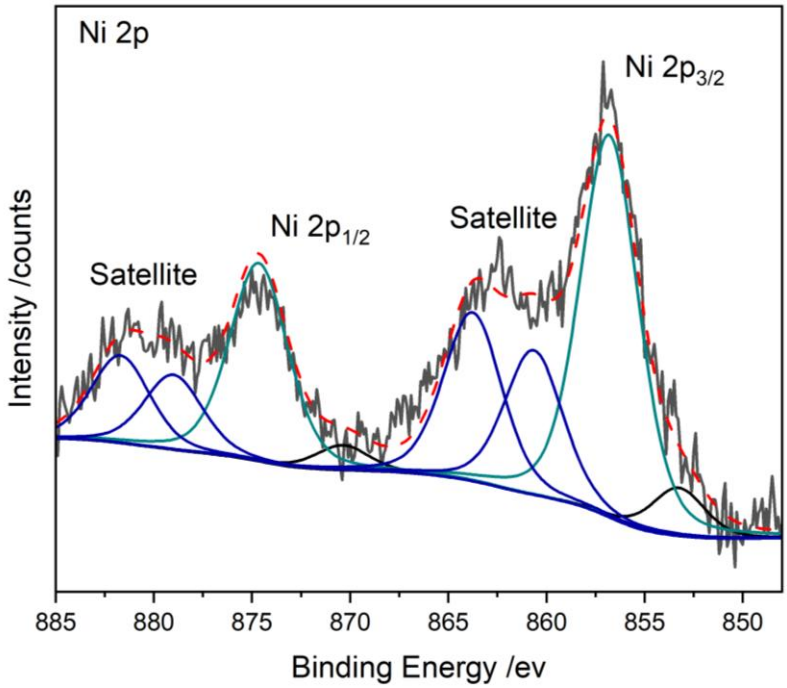

Figure 9. Ni 2P XPS spectrum of air-exposed catalyst **1**.

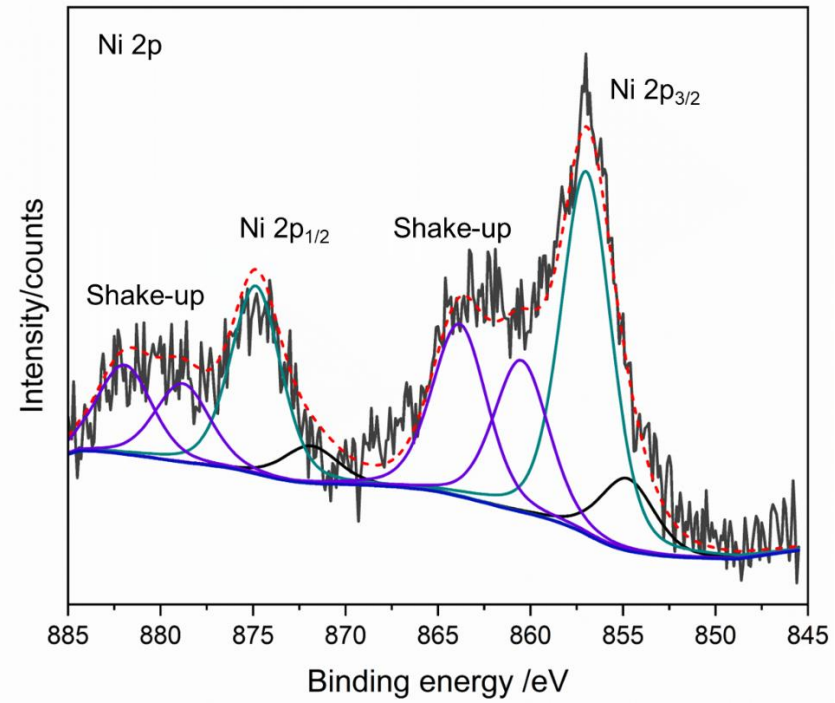

Figure 10. Ni 2P XPS spectrum of air-exposed spent catalyst.

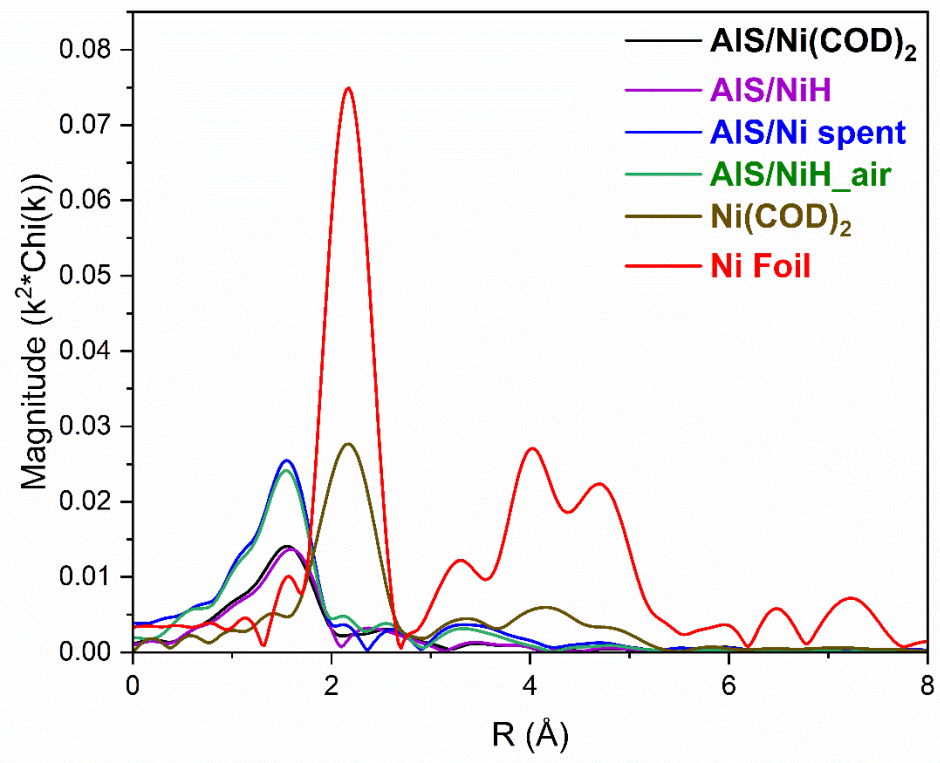

Figure 11. EXAFS k^2 magFT for Catalyst **1**, AlS/NiH, spent catalyst, air-exposed catalyst, $Ni(COD)_2$, and Ni foil.

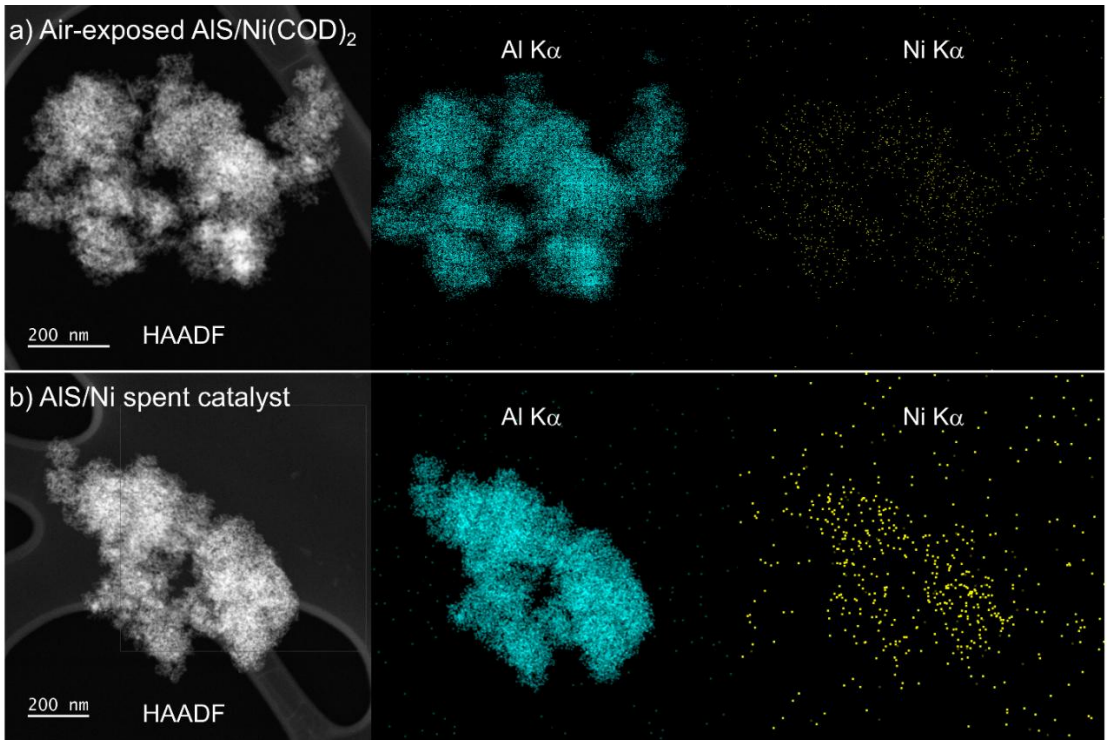

Figure 12. STEM- HAADF images and the corresponding elemental mapping of (a) air-exposed AlS/Ni(COD)$_2$ (b) AlS/Ni spent catalyst

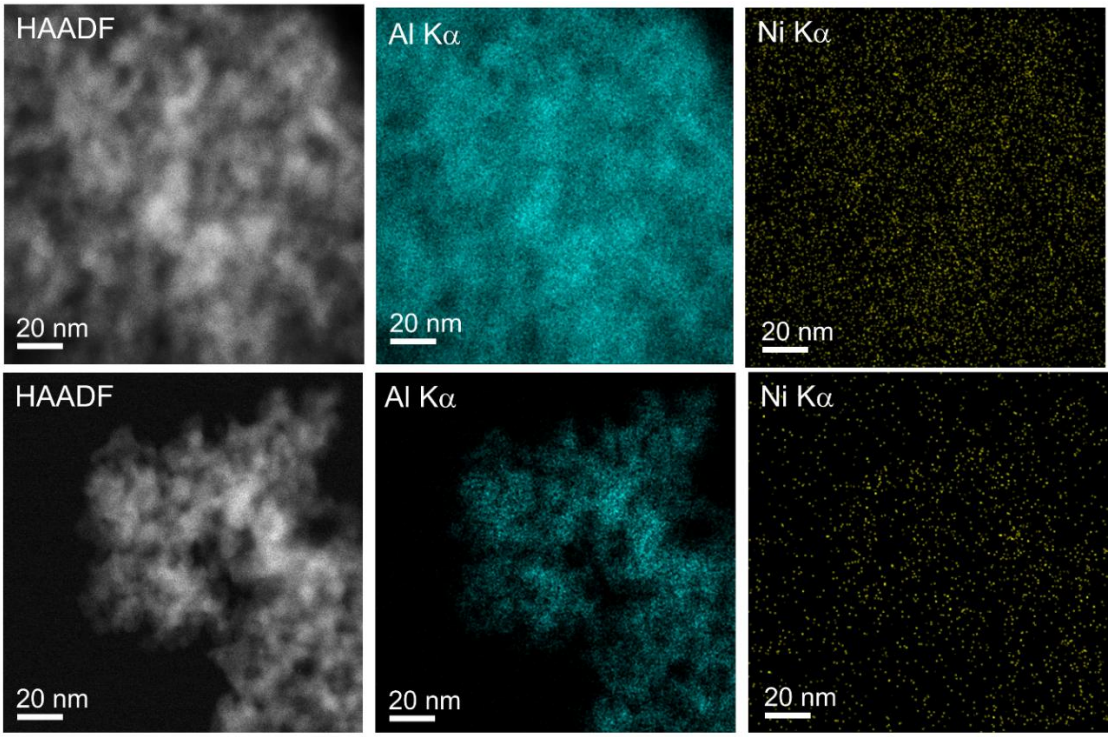

Figure 13. High-resolution STEM- HAADF images and the corresponding elemental mapping of AlS/NiH

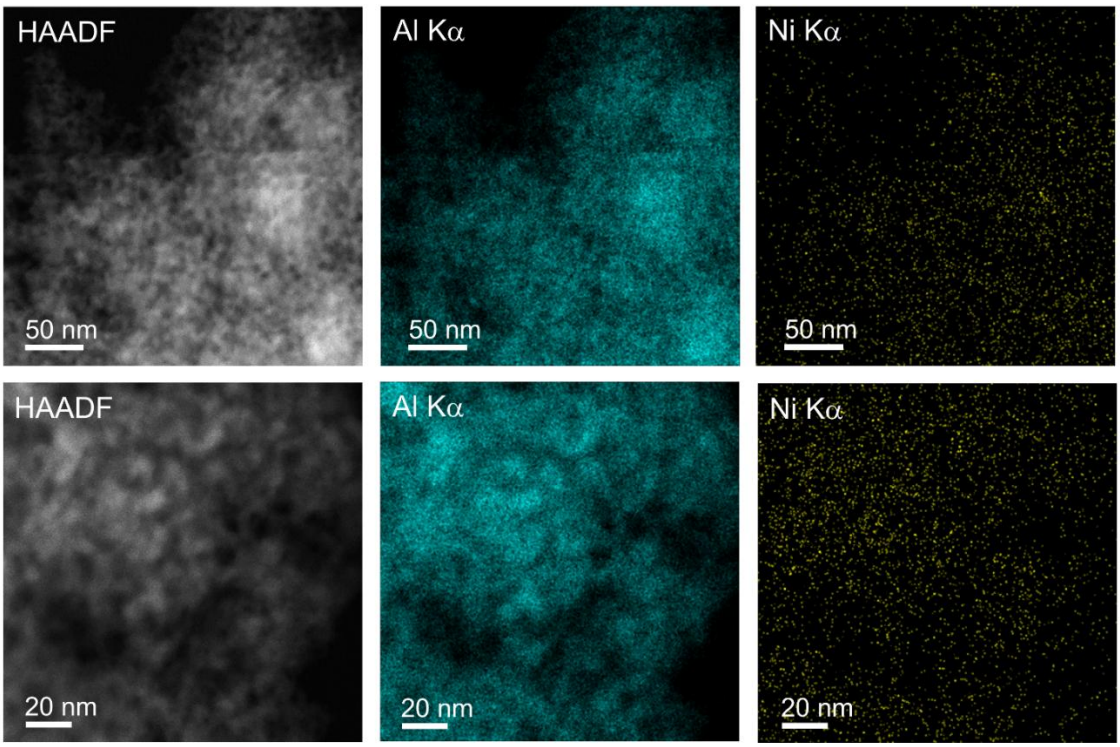

Figure 14. High-resolution STEM- HAADF images and the corresponding elemental mapping of AlS/Ni spent catalyst

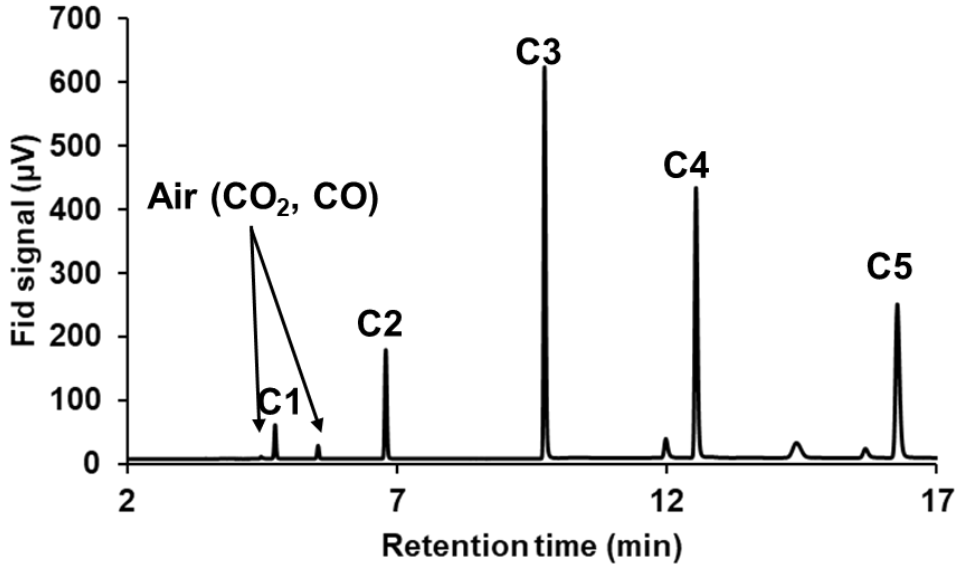

Figure 15. GC-fid chromatogram of gas phase sample of Lab-synthesized PE hydrogenolysis catalyzed by AlS/Ni$(COD)_2$

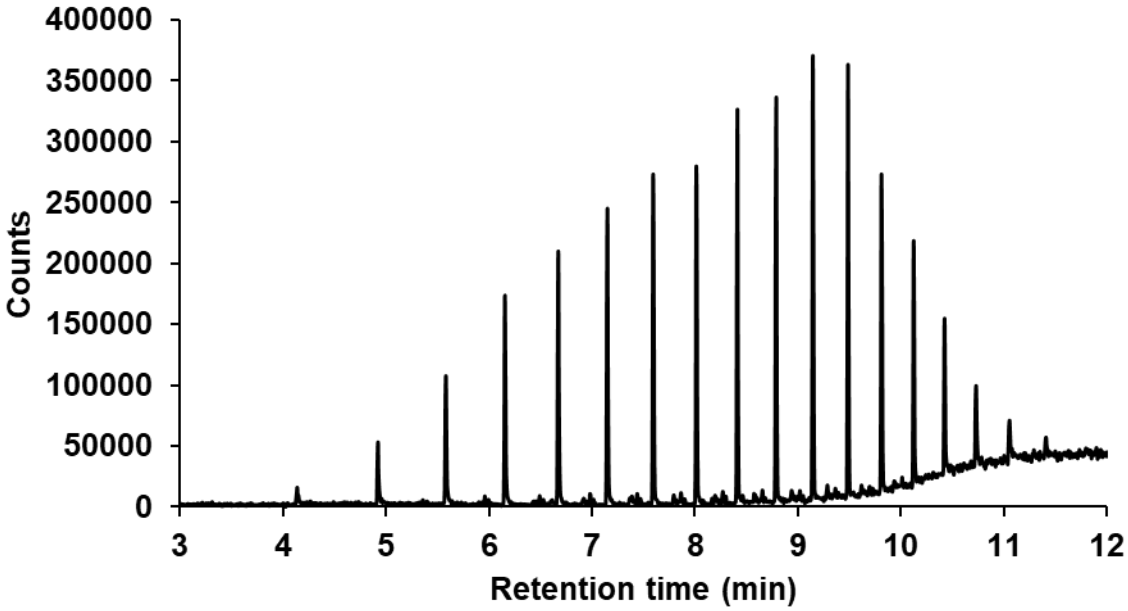

Figure 16. GC-MS chromatogram of DCM extract of Lab-synthesized PE hydrogenolysis catalyzed by AlS/Ni(COD)$_2$

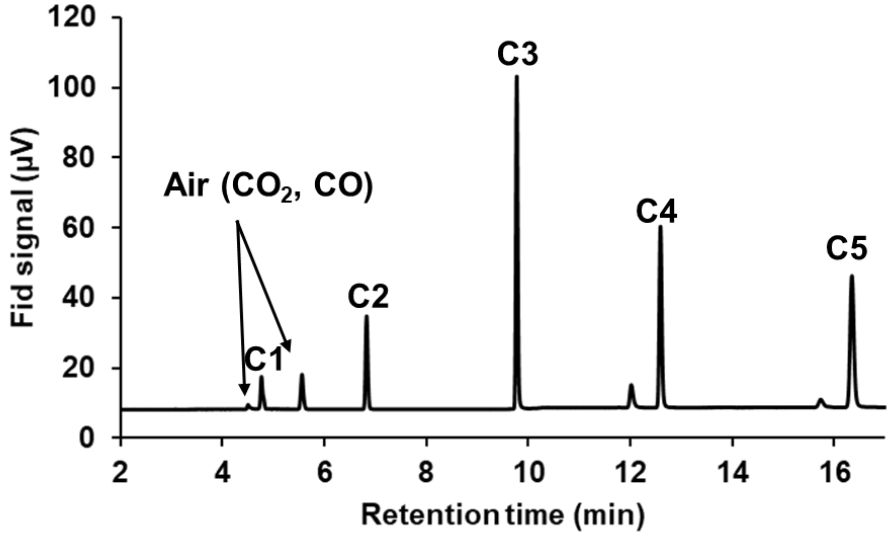

Figure 17. GC-fid chromatogram of gas phase sample of PECO hydrogenolysis (60 min) catalyzed by AlS/Ni(COD)$_2$

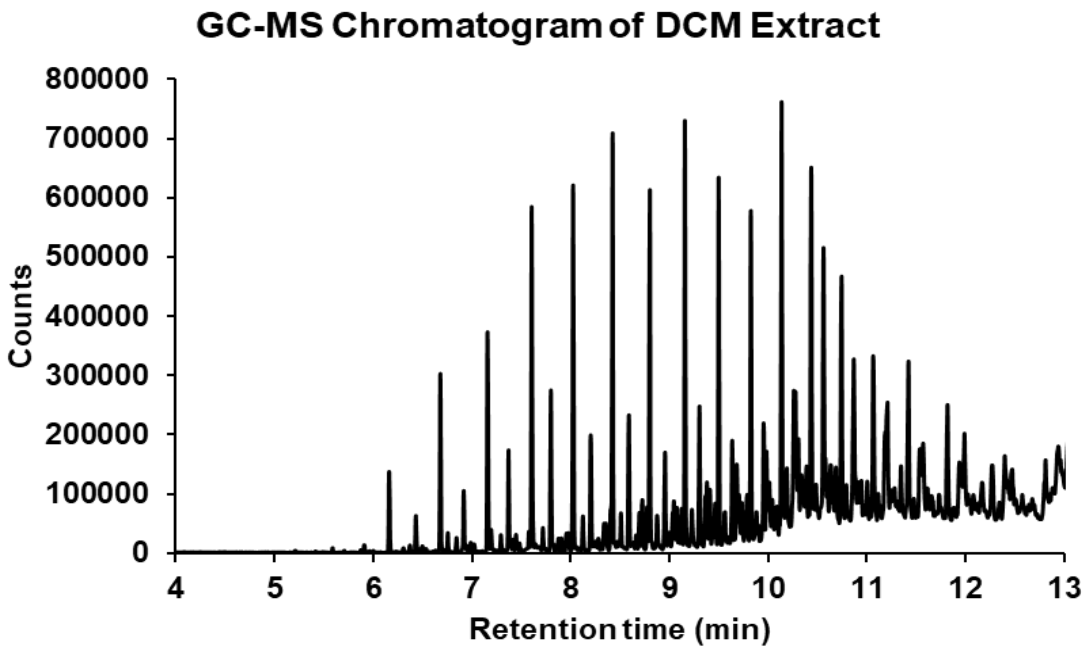

Figure 18. GC-MS chromatogram of DCM extract of PECO hydrogenolysis catalyzed by AlS/Ni(COD)$_2$

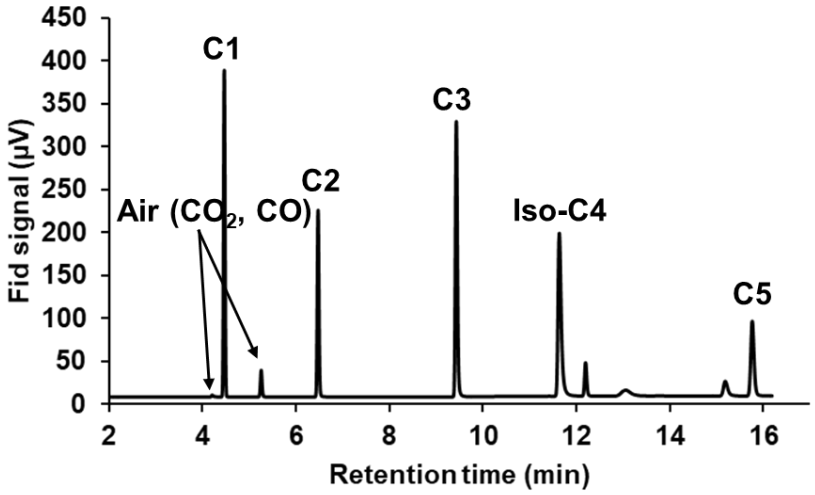

Figure 19. GC-fid chromatogram of gas phase sample of commercial *i*-PP hydrogenolysis catalyzed by AlS/Ni(COD)$_2$

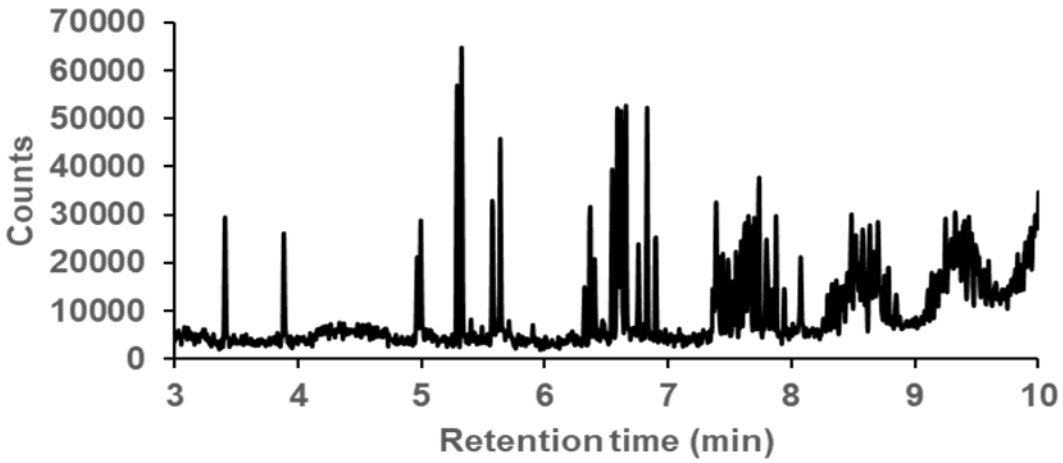

Figure 20. GC-MS chromatogram of DCM extract of *i*-PP hydrogenolysis catalyzed by AlS/Ni(COD)$_2$

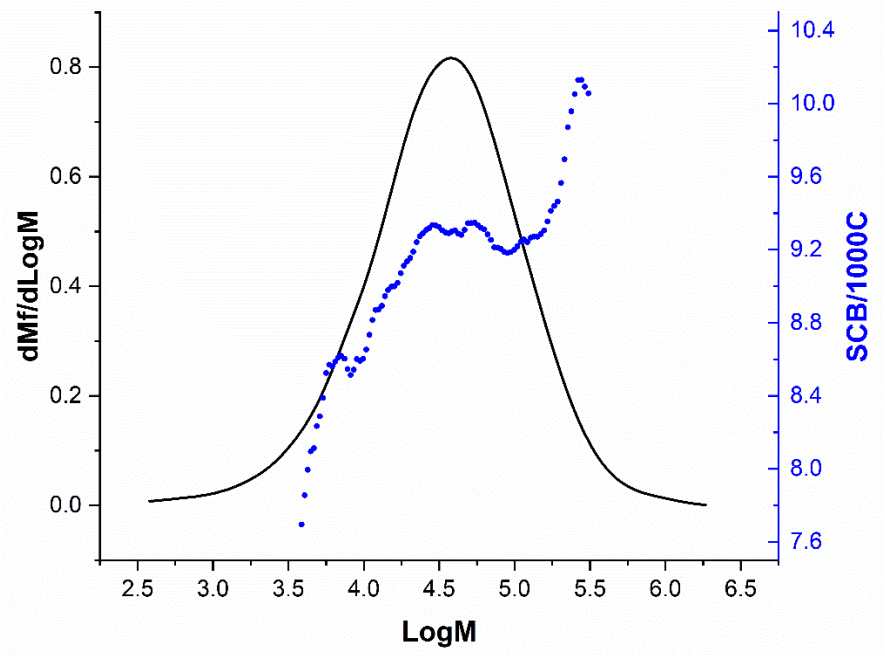

Figure 21. Short Chain Branching GPC (SCB/1000C) of linear PE (bottle cap)

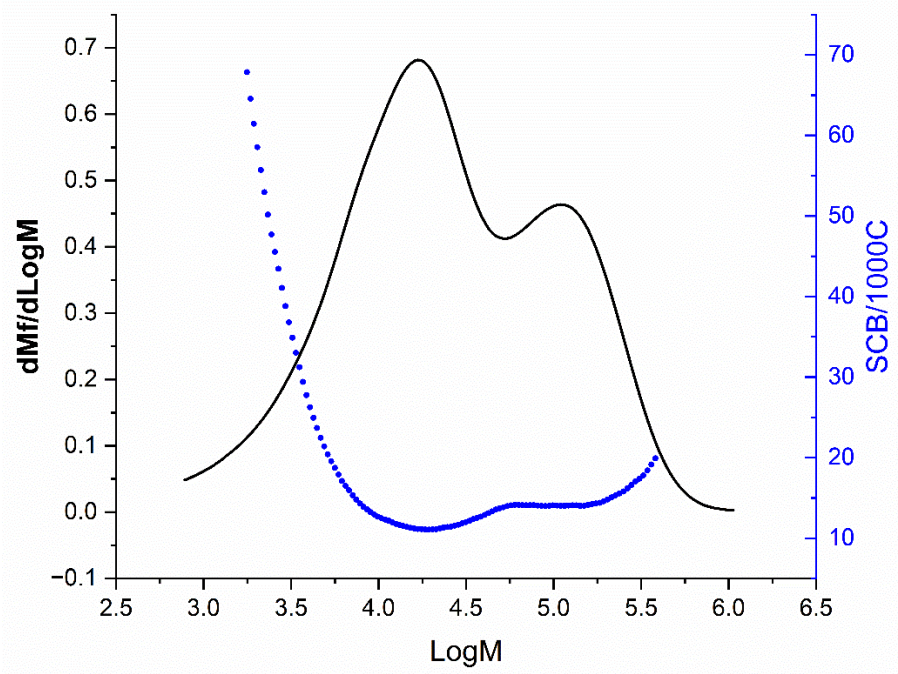

Figure 22. Short Chain Branching GPC (SCB/1000C) of the solid fraction recovered from hydrogenolysis of 19% PE + 81% *i*-PP mixtures

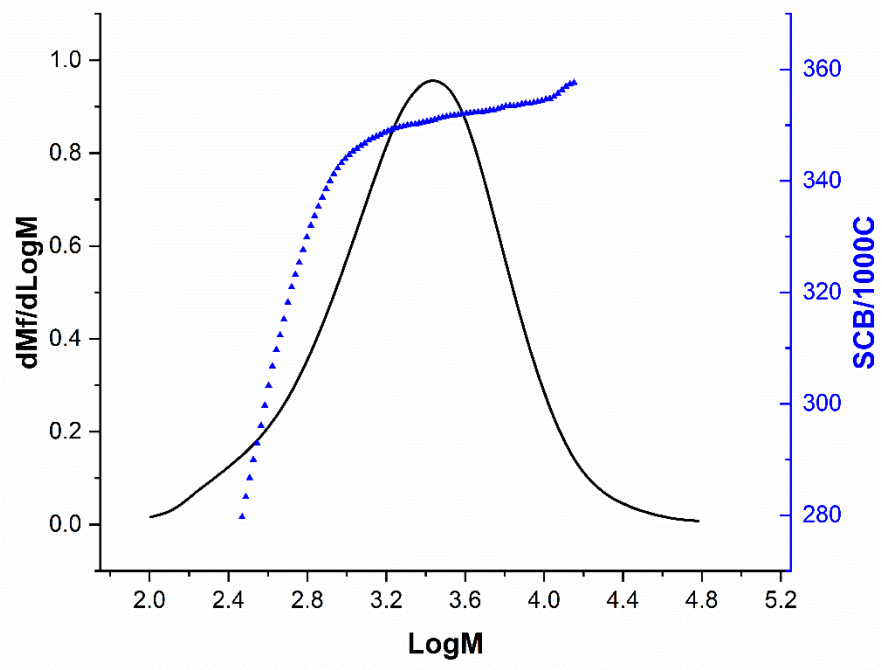

Figure 23. Short Chain Branching GPC (SCB/1000C) of DCM extract recovered from hydrogenolysis of 19% PE + 81% *i*-PP mixtures

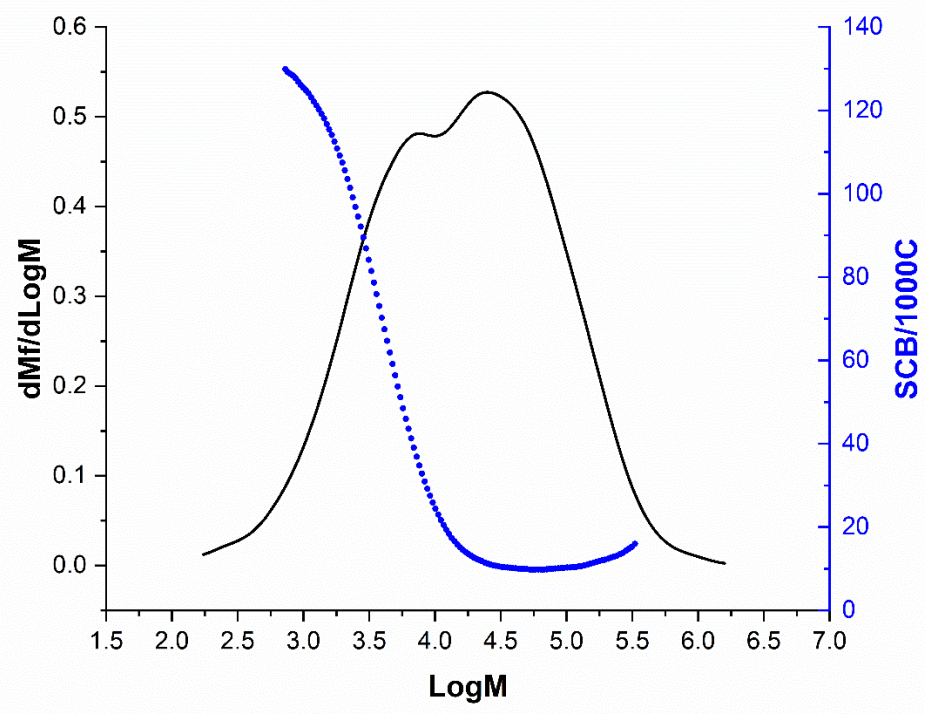

Figure 24. Short Chain Branching GPC chromatogram of solid fraction recovered from hydrogenolysis of 52% PE + 48% *i*-PP mixtures

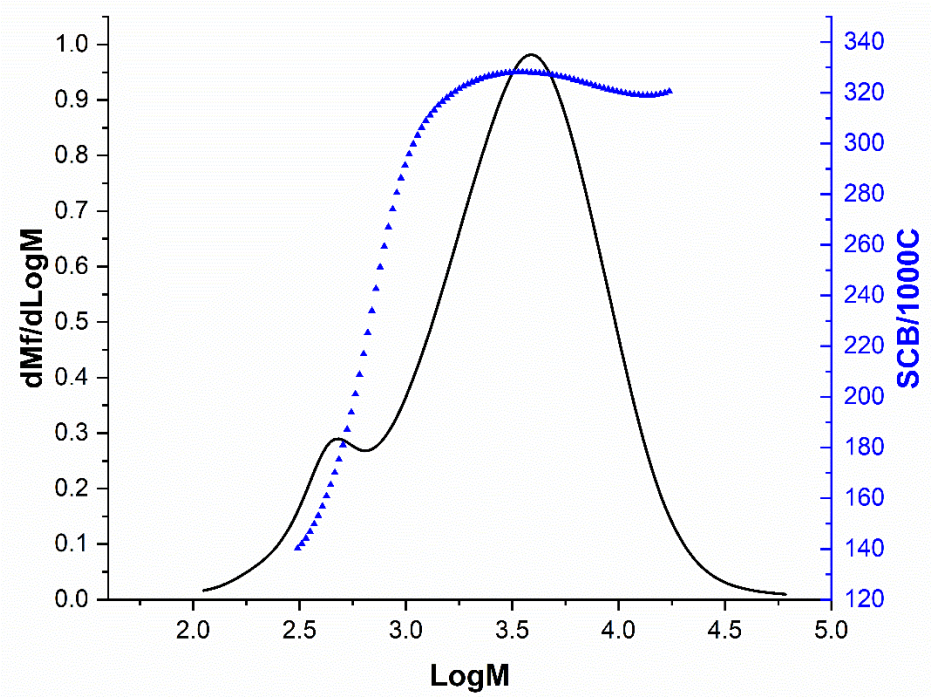

Figure 25. Short Chain Branching GPC chromatogram of DCM extract recovered from hydrogenolysis of 52% PE + 48% *i*-PP mixtures

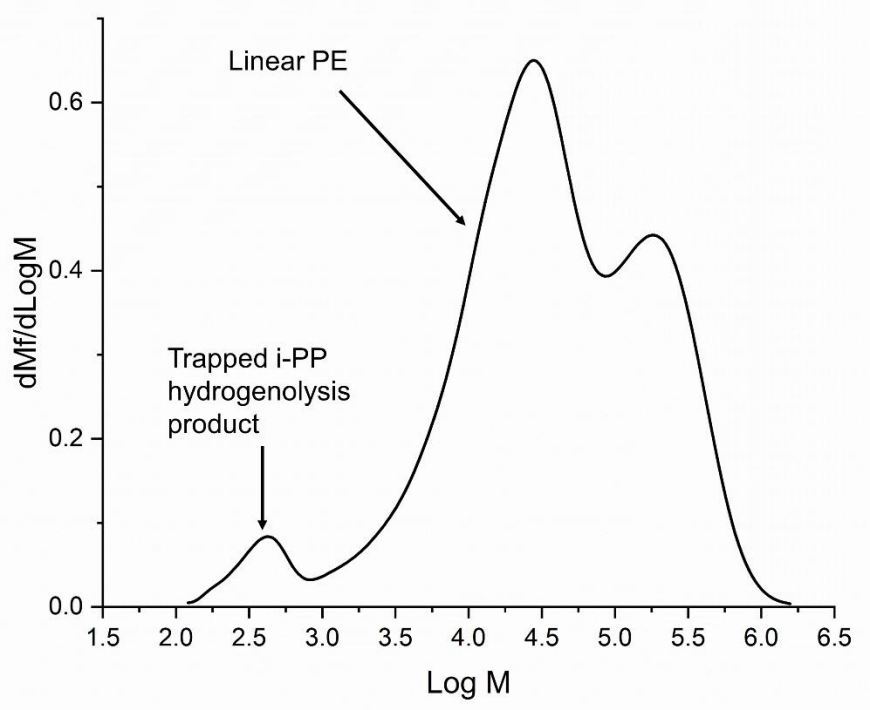

Figure 26. GPC chromatogram of solid fraction recovered hydrogenolysis of 19% PE + 81% *i*-PP mixtures for 1 h at 200 ˚C

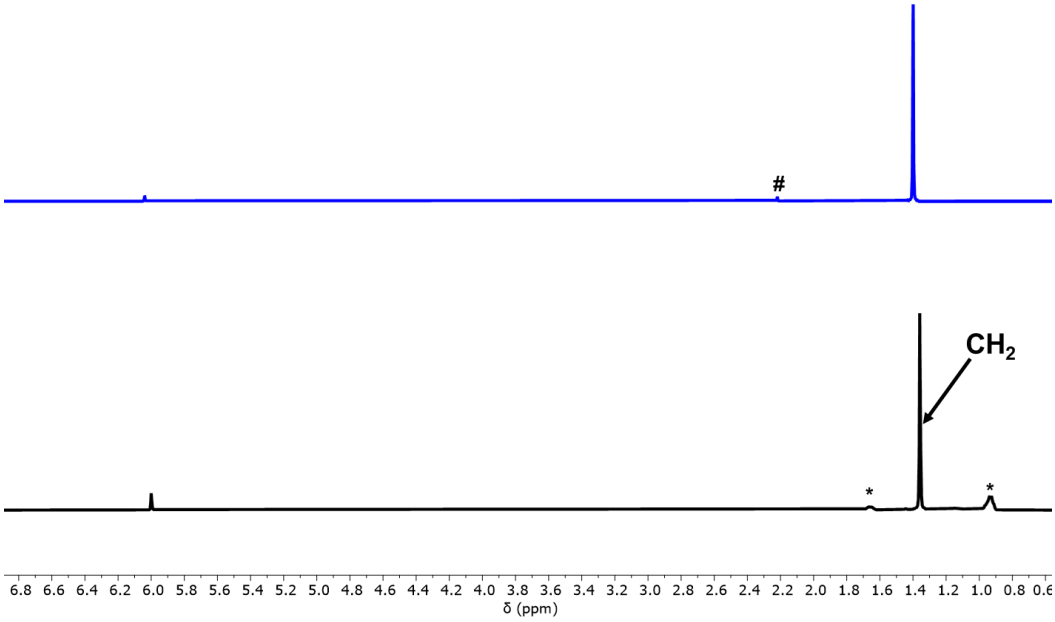

Figure 27. Stacked ^{1}H NMR{500 MHz, $CDCl_3$} spectra of unreacted HDPE (water bottle cap) and solids recovered after hydrogenolysis of *i*-PP + PE mixtures (adventitious acetone residue denoted by #, the *i*-PP hydrogenolysis product is denoted by *****).

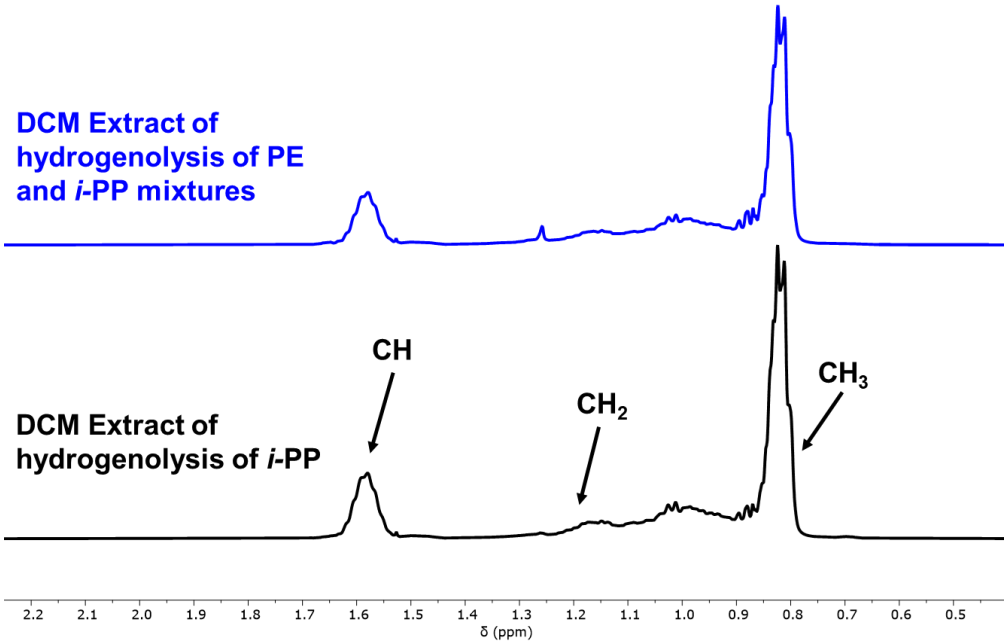

Figure 28. Stacked ^{1}H NMR {500 MHz, $CDCl_3$} spectra of DCM extract of stepwise hydrogenolysis of mixtures and *i*-PP hydrogenolysis.

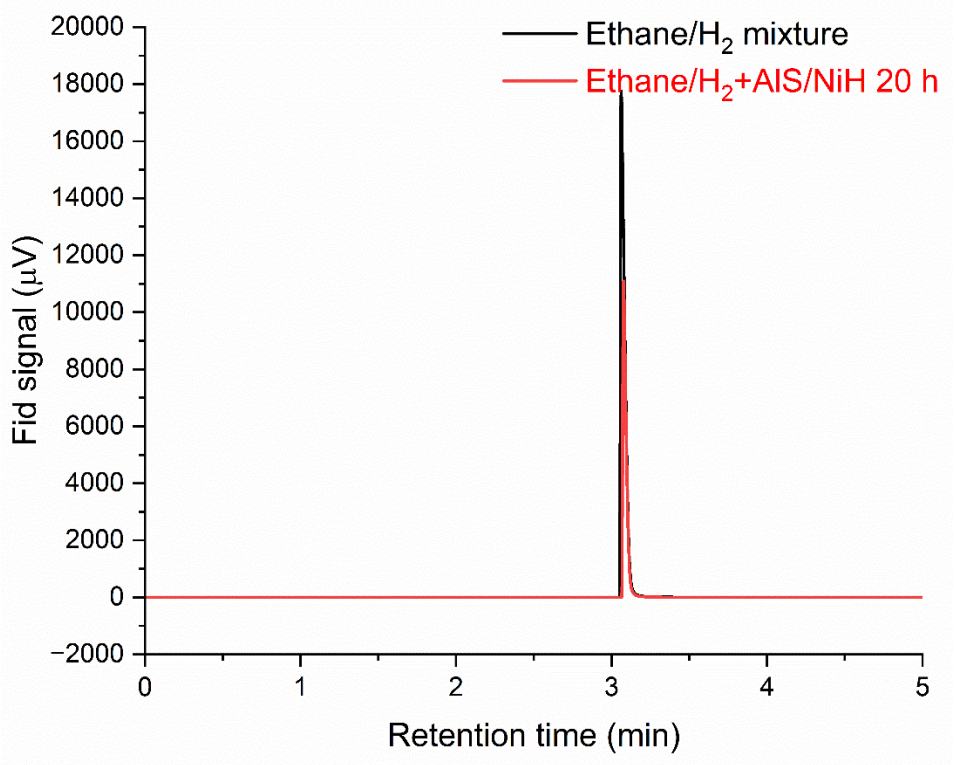

Figure 29. Stacked GC-fid chromatograms of Ethane/H_2 mixtures before and after attempted hydrogenolysis.

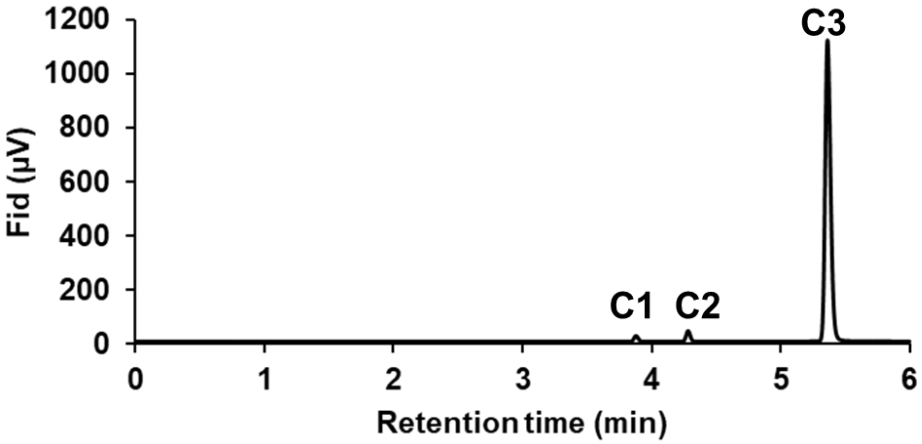

Figure 30. Typical GC-fid chromatogram of propane hydrogenolysis products from BenchCat flow reactor.

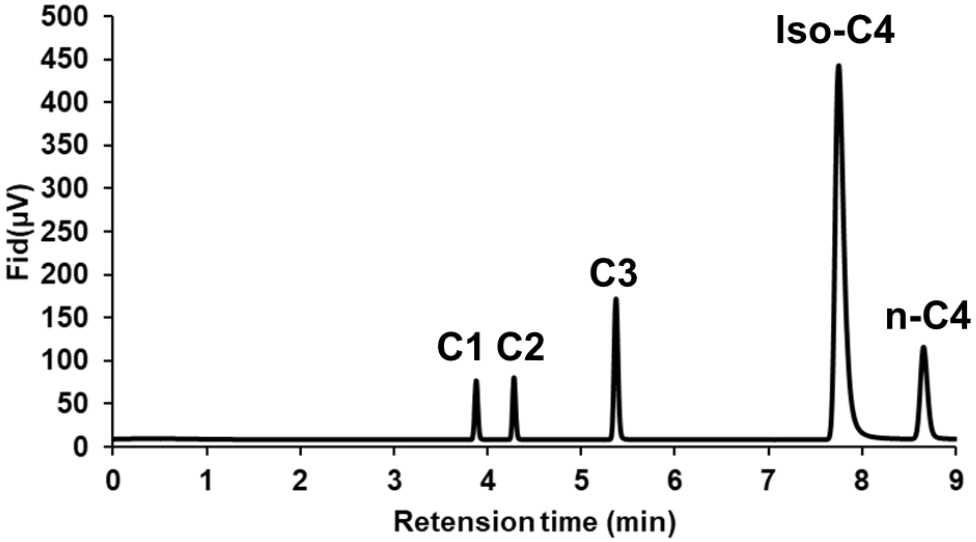

Figure 31. Typical GC-fid chromatogram of iso-butane hydrogenolysis products from BenchCat flow reactor.

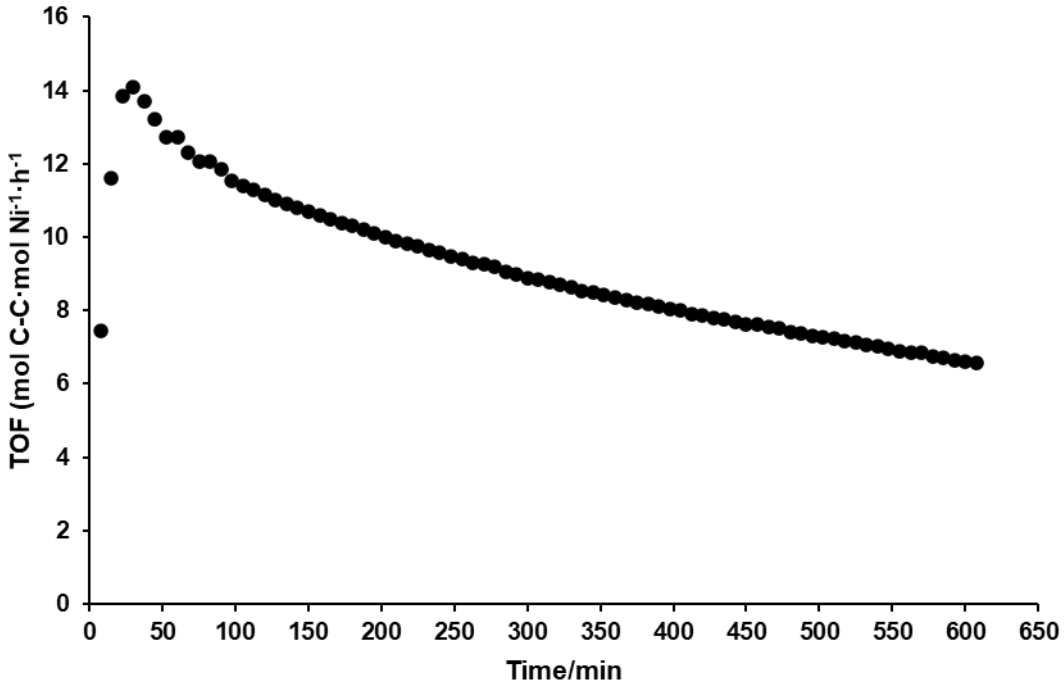

Figure 32. TOF vs time plot for propane hydrogenolysis at 200 °C (10 sccm 9.9% propane in Ar, 10 sccm H_2, 7.8 μmol Ni).

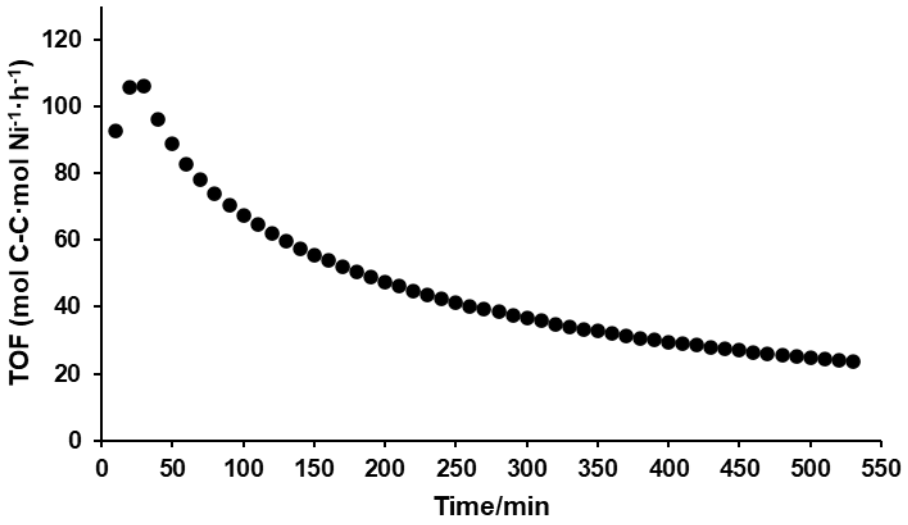

Figure 33. TOF vs time plot for iso-butane hydrogenolysis at 200 °C (10 sccm 9.9% iso-butane in Ar, 10 sccm H_2, 7.9 μmol Ni).

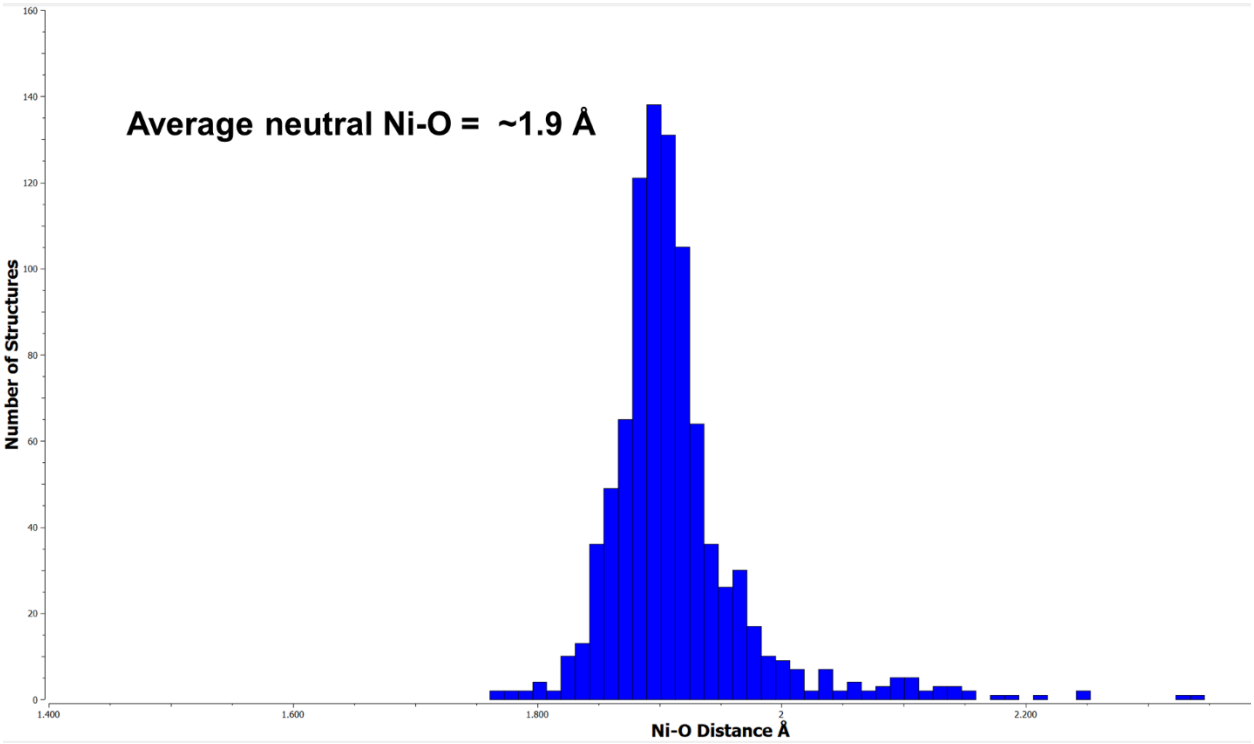

Figure 34. Statistical distribution of Ni-O bond distances in RNi-OR Type Complexes with at least one Ni-O bond. The statistical analysis performed using the Mercury software; the structures were obtained from the November 2023 Cambridge Structural Database release using the ConQuest software.

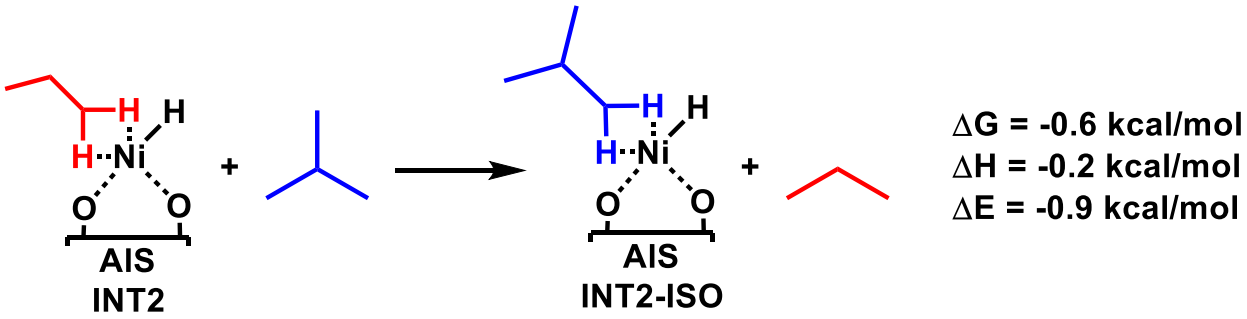

Figure 35. Isobutane/propane exchange reaction demonstrating a greater affinity for isobutane at the Ni center.

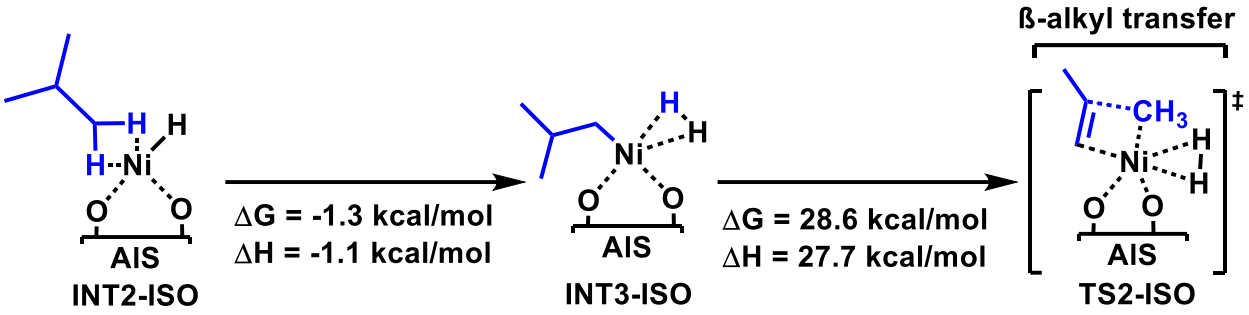

Figure 36. Calculated rate determining β-alkyl transfer step for isobutane.

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