Elucidating the Effect of Nanocube Support Morphology on the Hydrogenolysis of Polypropylene over Ni/CeO₂ catalysts

Supporting Information

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Materials

Ce(NO₃)₃.6H₂O (99%, Sigma Aldrich), CeO₂ nanopowder (<25 nm Sigma Aldrich), NiCl₂.6H₂O (99.9% Sigma Aldrich), NaOH (pellets, Fisher Scientific), ethanol (absolute, Fisher Scientific), dichloromethane (99.8%, Sigma Aldrich), isotactic polypropylene ($M_w \approx 12000$ g mol⁻¹, $M_n \approx 5000$ g mol⁻¹, Sigma Aldrich). All chemicals were used without further purification.

CeO₂ support synthesis

Shaped CeO₂ nanocubes were synthesised using a hydrothermal method.¹ Initially, Ce(NO₃)₃.6H₂O (2.1711 g) was dissolved in deionised water (20 ml) and added to a 9 M NaOH solution (60 ml) in a 125 ml PTFE liner. The resulting suspension was stirred for 30 min at room temperature and then the liner and suspension were placed into a steel autoclave and sealed. The sealed autoclaves were heated to 180 °C for 24 h. Once cooled, the resulting solid was collected by centrifugation (4000 RPM; 4 min) and washed with deionised water (3x30 ml) and ethanol (3x30 ml) and dried for 16 h at 80 °C. Finally, the materials were calcined in static air at 400 °C for 4 h.

Ni/CeO₂ catalyst synthesis

Ni/CeO₂ catalysts were prepared using a two-step impregnation method according to the literature.² For 2 g of catalyst with a theoretical 1 wt% Ni loading, NiCl₂.6H₂O (0.0810 g) was dissolved into ethanol (400 ml). CeO₂ (1.98 g) was dispersed in the Ni solution and sonicated for 10 mins. The solvent was removed using a rotary evaporator and the resulting solid was dried at 80 °C for 12 h. The dried solid was then calcined at 300 °C for 5 h (ramp rate: 5 °C min⁻¹) under static air. The solid was then washed and centrifuged (4000 RPM, 4 min) with a 1:1 water to ethanol solution (3 x 30 ml) and dried at 80 °C for 12 h. A final calcination at 500 °C for 5 h (ramp rate: 1 °C min⁻¹) under static air in a box furnace was then conducted to yield the catalyst.

Catalyst characterisation `

Synchrotron powder X-ray diffraction (PXRD) was undertaken at Diamond Light Source on high resolution beamline I11 ($\lambda = 0.825479$ Å) under the proposal CY31578. The patterns were collected in transmission mode ($0^{\circ} < 2\theta < 95^{\circ}$) using a position sensitive detector (PSD) at room temperature. Samples were prepared with an amorphous carbon black diluent and loaded into 0.5 mm diameter borosilicate glass capillaries. Air sensitive samples (reduced Ni/CeO₂) were prepared in a glovebox and torch sealed. Pawley fitting of samples was carried out using TOPAS Academic V5 to determine lattice parameters and cell volume of cubic CeO₂, with models of background and instrument parameters, and Pseudo-Voight peak types. Patterns were matched and fitted using a ICSD database crystal structure of CeO₂ (ICSD collect code 72155).³ Crystallite sizes were calculated using the Scherrer equation from the FWHM of individually fitted peaks with Pseudo-Voight peak types.

Inductively coupled plasma-optical emission spectrometry (ICP-OES) was undertaken to determine Ni loading on the catalysts and measured using an Agilent 5110 ICP-OES instrument. Liquid samples for analysis were prepared by dissolution of solid samples (0.025 g) in 37% hydrochloric acid (10 ml) in a 23 ml Parr 4749 PTFE lined acid digestion vessel and heated to 200 °C for 6 h. The resulting solution was diluted to 50 ml before ICP-OES analysis.

 N_2 adsorption-desorption isotherms were performed at -196 °C using a Micromeritics Tristar II. Prior to analysis, the samples were degassed overnight at 120 °C. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo NEXSA XPS fitted with a monochromated Al ka X-ray source (1486.7 eV), a spherical sector analyser and 3 multichannel resistive plate, 128 channel delay line detectors. All data was recorded at 19.2 W and an X-ray beam size of $200 \times 100 \,\mu\text{m}$. Survey scans were recorded at a pass energy of 160 eV, and high-resolution scans recorded at a pass energy of 20 eV. Electronic charge neutralisation was achieved using a Dual-beam low-energy electron/ion source (Thermo Scientific FG-03). Ion gun current = 150μ A. Ion gun voltage = 45 V. All sample data was recorded at a pressure below 10^{-8} Torr and a room temperature of 294 K. Air sensitive reduced samples were introduced by inert transfer from a glovebox. Data was analysed using CasaXPS v2.3.25PR1.0. Spectra were charge corrected to adventitious carbon at 284.8 eV. Peaks were fit with a Shirley background prior to component analysis. An offset Shirley background was used to fit the Ce 3d spectrum. Voight-like functions were used for symmetric line-shapes (LA(1.53, 243)) and were used to fit Ce(III), O 1 s, and C 1 s components. Asymmetric-like line shapes (LA(0.9,2,50)) were used to fit Ce(IV), as developed by Morgan et al.⁶ The Ce 3d region was fit with a 10-component model according to the literature.⁴⁻⁶ The complex Ce 3d spectrum arises from various initial and final state effects derived from ligand-to-metal transfer. For CeO₂, with Ce(IV), there is a total of 6 peaks, where u, v, uⁱⁱ, and vⁱⁱ arise from the Ce Ce 3d⁹4f⁰ O 2p⁴ and Ce 3d⁹4f⁰ O 2p⁵ states. Whereas uⁱⁱⁱ and vⁱⁱⁱ peaks arise from Ce 3d⁹4f⁰ O 2p⁶ final state. The Ce₂O₃ contribution, with Ce(III), exhibits 4 peaks corresponding to the Ce 3d⁹4f¹ O 2p⁶ final state with peaks uⁱ and vⁱ, and peaks u⁰ and v⁰ from the Ce 3d⁹4f² O 2p⁵ final state.⁴⁻⁶ Peak positions are given in Table S9 with corresponding notation. Following an initial fit of the peak model based on literature values, slight relaxation of FWHM, area, and binding energy constraints were allowed to account for distortions arising from heterogenous defects and differences in instruments between studies.⁷ Atomic percentages were calculated using the highresolution scans of Ce 3d, C 1 s/Ce 4 s, Ni 2p, and O 1 s. The Ce(III) percentage was calculated using the ratio of peak areas of the Ce 3d region. No other major species were noted in the survey scans including Na, which potentially arises from the synthesis method and indicates the washing step in CeO₂ synthesis is sufficient to remove impurities.

Ni k-edge X-ray absorption spectra (XAS) were collected in fluorescence mode on the B18 beamline at Diamond Light Source using a Si (311) monochromator. Access to the beamline was obtained through block allocation group (BAG) access via the UK Catalysis Hub (Proposal SP29271). All samples (Ni/CeO₂-SA and Ni/CeO₂-NC fresh and post 16 h reaction) were pressed into a pellet using cellulose as a diluent. The XAS data and the extended X-ray absorption fine structure (EXAFS) were processed and fitted using IFEFFIT with the Horae package (Athena and Artemis).⁸ The fit range for the EXAFS data was $3 < k < 10 \text{ A}^{-1}$, 1.0 < R < 3.3 Å. Scattering paths were initially determined from FEFF calculations of crystal structures (NiO and Ni) from the ICSD database, with Ni-O₆ and Ni-Ni(1) single scattering paths calculated from NiO (ICSD collect code 9866) and a separate Ni-Ni(2) single scattering path from Ni(0) (ICSD collect code 37502).^{9,10} In the fitting of measured bulk standards, coordination numbers were not floated, assuming purely crystalline bulk samples. In the fitting of the catalysts, the 1st shell Ni-O CN was fixed at 6 with floating of the disorder parameter ($2\sigma^2$), as a large deviation from the ideal CN is not anticipated for the first shell of metal oxides in correspondence with literature, and to limit variable parameters when fitting additional shells.^{11,12} Consideration of any deviations from Ni-O₆ can be captured in any alterations of the structural disorder parameter.

Temperature programmed reduction (TPR) measurements were performed using an Altamira AMI-300 Lite equipped with a Drierite trap. Materials (approximately 0.06 g; exact measurements recorded for each experiment) were loaded in-between quartz wool and reduced under 5% H₂/Ar under a flow rate of 50 SCCM with a 10 °C min⁻¹ ramp rate from 30-1000 °C. Hydrogen consumption was measured by a thermal conductivity detector (TCD), with calibrations conducted by multiple argon pulses through a 574 μ L sample loop (TCD settings: current = 75 mA, TCD gain = 10, signal sample rate = 0.1 sec/pt).

Analysis of component contributions was undertaken after background subtraction and fitting with Lorentzian line shapes. CeO_2 analysis was deconvoluted using three peaks associated with multi-stage surface and bulk reduction. Whereas Ni/CeO₂ catalysts were fitted with four peaks affiliated to Ni reduction and CeO₂ reduction. Component analysis was kept consistent between samples to minimise errors.

Temperature programmed desorption (TPD) measurements using an Altamira AMI-300 Lite. CO₂ was used to probe basic site whereas NH₃ was used to analyse acid sites, with desorption measured using a TCD (TCD settings: current = 180 mA, TCD gain = 20, signal sample rate = 0.1 sec/pt). Calibrations were conducted using multiple pulses of CO₂ or 10% NH₃/He through a 574 μ L sample loop. Measurements were performed on approximately 0.3 g material to ensure appreciable signal. A furnace thermocouple was used to measure the temperature. Exact measurements recorded for each sample of fresh or surface reduced CeO₂-SA and CeO₂-NC. Pretreatment was undertaken with He or 5%H₂/Ar before dosing with probe molecules. He pre-treatments (flow rate: 50 SCCM) were performed at 200 °C for 1 h (ramp rate: 10 °C min⁻¹), whereas 5% H₂/Ar treatments (flow rate: 50 SCCM) were carried out at 550 °C for 30 min (ramp rate: 10 °C min⁻¹) and cooled under gas flow. Following pre-treatment, the samples were saturated (flow rate: 30 SCCM) with probe gas (CO₂ or 10% NH₃/He) for 30 min at 30 °C. Any excess and physisorbed probe gas was then removed with He flow (flow rate: 30 SCCM) for 30 min prior to measurement. TPD measurements were then conducted from 30 °C to 600 °C (ramp rate: 10 °C min⁻¹) and held for 1 h under He flow (flow rate: 30 SCCM).

TPD measurements of 2,2,4-Trimethylpentane (2,2,4-TMP) probe were undertaken on a Micromeritics Autochem 2920 II equipped with a TCD and vapour generator. Measurements were performed on approximately 0.3 g material to ensure appreciable signal. A bed thermocouple was used to measure the temperature. Exact measurements recorded for each sample of fresh or surface reduced CeO₂-SA and CeO₂-NC. He pre-treatments (flow rate: 50 SCCM) were performed at 200 °C for 1 h (ramp rate: 10 °C min⁻¹) and cooled under gas flow. Following pre-treatment, the samples were saturated (flow rate: 30 SCCM) with 2,2,4-TMP at 40 °C by dosing multiple times. Any excess 2,2,4-TMP was removed with He flow (flow rate: 30 SCCM) for 30 min prior to measurement. TPD measurements were then conducted from 40 °C to 700 °C (ramp rate: 10 °C min⁻¹). High Angle annular Dark Field (HAADF) and Bright Field (BF) Scanning Transmission Electron Microscopy (STEM) imaging were performed using an aberration corrected JEOL 2100FCs microscope operating at 200 kV.

Catalyst reactions without polymer

Reactions to study catalyst speciation under reaction conditions were carried out using a 100 ml Parr 5500 series reactor with a 4848-control system. Catalyst (0.2 g) was loaded into a glass liner and placed into the autoclave and sealed. The reactor was flushed multiple times with N₂ and pressurised with pure H₂ at room temperature to 20 bar and heated to 280 °C (~30 bar *P*H₂ at reaction temperature) for 8 h. Upon cooling the reactor, the gases were vented, and the reactor was flushed with N₂. The sealed reactor was transferred to the glovebox and the catalyst was removed and stored. Analysis of the reduced catalyst was undertaken using XPS and synchrotron PXRD following sealing and further inert transfer.

Catalyst testing

The hydrogenolysis of polypropylene was carried out using a 100 ml Parr 4590 series reactor with a 4848-control system. In a typical reaction, 2 g of polypropylene ($M_w \approx 12,000$ Da, $M_n \approx 5000$ Da) and catalyst with fixed 0.00138 g of Ni (0.4 wt% Ni/CeO₂-SA (0.364 g); 0.7 wt% Ni/CeO₂-NC (0.2 g); 1.2 wt% Ni/CeO₂-SA (0.1123 g)) was loaded into a glass liner in the autoclave. Blank reactions were undertaken without catalyst or support and reactions with supports were carried out using CeO₂ (0.2 g).

The reactor was then sealed and flushed multiple times with N₂ and followed by flushing with H₂. The reactor was then pressurised with H₂ at room temperature to 20 bar and heated to 280 °C (~30 bar *P*H₂ at reaction temperature) for the allotted reaction time (8-24 h) with a stirring rate of 500 RPM. Upon cooling the reactor, the gases in the headspace were analysed using an online Agilent 8860 GC equipped with an FID detector and a CP-Sil 8 CB column (50 m X 0.32 mm X 5 μ m). After the excess gas was vented, the catalyst, solid and liquid products were extracted using dichloromethane (30 ml) and filtered. The solid fraction was dried at room temperature overnight. The liquid fraction was collected by evaporation of the solvent using a rotary evaporator. All products were measured gravimetrically, with yields calculated using mass fractions.

Liquid analysis

The number average (M_n) , weight average (M_w) , peak molecular weight (M_p) , and dispersity (D) were calculated from the measurement of liquids in gel permeation chromatography (GPC) The GPC analyses were performed using an Agilent Technologies 1260 Infinity II equipped with a refractive index (RI) detector and a Viscotek T3000 + T2000 + guard column set with a mobile phase of THF at 35 °C and a flow rate of 1 mL min⁻¹. All samples were dissolved at 10 mg mL⁻¹ and passed through a 0.2 µm PTFE syringe filter prior to injection (100 µL). Narrow polystyrene standards (Polymer Standards Service (PSS), $M_p = 162$, 1098, 4840 and 9630 g mol⁻¹) were used to construct a conventional calibration curve to which all samples were compared.

Thermogravimetric analysis (TGA) of the produced liquids was carried out using a TA SDT Q600 to investigate the oxidation profile of liquids. The samples were heated under flowing air (50 ml min⁻¹) to 600 °C, with a ramp rate of 10 °C min⁻¹.

Reaction calculations

Conversion and product yields

Solid conversion was calculated using the following equation:

$$C_{solid}(\%) = 100 \times \frac{m_{PP} - m_{solid} - m_{cat}}{m_{PP}}$$
 (Equation S1)

Where C_{solid} is conversion of solid, as solid refers to both unreacted and reacted polymer, m_{PP} is the mass of polypropylene, m_{solid} is the gravimetrically measured mass of solid residue after drying overnight, m_{cat} is the mass of catalyst used in the reaction, assuming no dissolution of catalyst.

Product yields are calculated using the following equation:

$$Y_{Product}(\%) = 100 \times \frac{m_{product}}{m_{pp}}$$
 (Equation S2)

Where $Y_{Product}$ is the yield of product and is either solid, liquid or gas, $m_{product}$ is the mass of product measured, m_{PP} is the mass of polypropylene. In this calculation, $m_{product}$ is determined gravimetrically, with mass of solid and liquid determined after drying and evaporation of solvent. The mass of gas is calculated from the residual mass, assuming mass balance of 100%.

Liquid productivity

Liquid productivities were calculated using the following equation:

$$P_{liquid}\left(g_{liquid} \ g_{Ni}^{-1} \ h^{-1}\right) = m_{liquid} \times \frac{1}{m_{Ni}} \times \frac{1}{t} \left(\text{Equation S3}\right)$$

Where P_{liquid} is the productivity of liquid normalised by mass of Ni and reaction time, m_{liquid} is the gravimetrically measured mass of liquid after rotary evaporation of solvent, m_{Ni} is the mass of Ni used in the reaction, t is the specified reaction time.

Average rate of carbon-carbon bond scission

The average rate of C-C scission normalised per mass of Ni $(r_{c-c} m_{Ni}^{-1})$ was calculated to an adjusted method reported by Lamb *et al.*¹³ using the following equations:

$$N(t) = \sum_{1}^{5} n_{gas} + \frac{m_{liquid}}{M_{n\,(liquid)}} + \frac{m_{solid}}{M_{n\,(PP)}}$$
(Equation S4)

$$N(0) = \frac{m_{pp}}{M_{n(PP)}}$$
(Equation S5)

 $r_{\mathcal{C}-\mathcal{C}} \ (mmol \ h^{-1}) = \frac{N(t) - N(0)}{t} \ (Equation \ S6)$

$$r_{\boldsymbol{C}-\boldsymbol{C}} m_{Ni}^{-1} \left(mmol \ g_{Ni}^{-1} h^{-1} \right) = \frac{r_{\boldsymbol{C}-\boldsymbol{C}}}{m_{Ni}} \left(\text{Equation S7} \right)$$

Where $\sum_{1}^{5} n_{gas}$ refers to the sum of gas (C₁-C₅) moles, m_{liquid} is the gravimetrically measured mass of liquid after rotary evaporation of solvent, $M_{n \ (liquid)}$ is the number average molecular weight of the produced liquid at specified reaction time, m_{solid} is the gravimetrically measured mass of solid residue after drying overnight, $M_{n \ (PP)}$ is the number average molecular weight of the initial PP, t is the specified reaction time, and m_{Ni} is the mass of Ni used in the reaction.

This calculation includes the thermal decomposition of the initial polymer, although, this is consistent between reactions and is a parameter of the process. The $M_{n(PP)}$ is taken from manufacturers values $(M_{n(PP)} \sim 5000 \text{ g mol}^{-1})$ due to inability to analyse initial polymer using the GPC instrument configuration. Additionally, the m_{Gas} is determined from residual mass balance and therefore the calculation of r_{C-C} carries forward small errors, although, the r_{C-C} is calculated for each repeat reaction and averaged.

Average M_w depolymerisation rate

The average M_w depolymerisation rate was calculated using the following equations:

$$M_{w(t)}(kg\ mol^{-1}) = \frac{(M_{w(PP)} - M_{w(liquid)})}{1000}$$
 (Equation S8)

Where $M_{w (PP)}$ is the weight average molecular mass of the initial PP, $M_{w (liquid)}$ is the weight average molecular mass of the liquid produced at the specified time, $M_{w (t)}$ is the depolymerisation expressed in weight average molecular mass of the initial polymer.

$$r_{M_{W(t)}}(kg \ mol^{-1} \ g_{Ni}^{-1} \ h^{-1}) = M_{W(t)} \times \frac{1}{m_{Ni}} \times \frac{1}{t}$$
 (Equation S9)

Where $r_{M_{w(t)}}$ is the average weight average molecular mass depolymerisation rate, $M_{w(t)}$ is the depolymerisation expressed in weight average molecular mass of the initial polymer, m_{Ni} is the mass of Ni used in the reaction, t is the specified reaction time.

This calculation does not include product yields and therefore is an indicative measure of internal cleavage rates rather than overall process rates, which is measured using the average rate of carbon-carbon scission. The $M_{w(PP)}$ taken from manufacturers values ($M_{w(PP)} \sim 12,000 \text{ g mol}^{-1}$) due to inability to analyse initial polymer using the GPC instrument configuration.

Catalyst	Time	Solid	Product yield (%)			GPC liquid analysis			
	(h)	conversion (%)	Solid	Liquid	Gas	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	Ð	$M_p(\mathbf{g} \mathbf{mol}^{-1})$
	8	24 (±3)	76 (±3)	9 (±3)	15 (±6)	-	-	-	-
-	16	22 (±3)	78 (±3)	9 (±2)	13 (±5)	-	-	-	-
	24	29 (±1)	71 (±1)	16 (±4)	13 (±3)	819 (±24)	1664 (±145)	2.03 (±0.12)	883 (±97)
CeO ₂ -SA	24	22 (±1)	78 (±1)	10 (±4)	12 (±4)	831 (±123)	1898 (±253)	2.03 (±0.23)	1095 (±94)
CeO ₂ -NC	24	28 (±3)	72 (±3)	9 (±4)	19 (±7)	726 (±3)	1603 (±12)	2.21 (±0.02)	617 (±0)

Table S1. PP hydrogenolysis reaction data for blank and support reactions. Hydrogenolysis reaction conditions: PP (2 g), CeO₂ (0.2 g), 280 °C, 30 bar H₂, 500 RPM, 8-24 h. Parenthesises show the standard deviation of multiple reactions. (SA – Sigma Aldrich; NC – nanocube).

Table S2. PP hydrogenolysis reaction data for Ni/CeO₂ catalytic reactions. Hydrogenolysis reaction conditions: PP (2 g), Ni/CeO₂ (fixed Ni content 0.00138g), 280 °C, 30 bar H₂, 500 RPM, 8-24 h. Parenthesises show the standard deviation of multiple reactions. (SA – Sigma Aldrich; NC – nanocube).

	Time Solid		Product yield (%)			GPC liquid analysis			
Catalyst	(h)	conversion (%)	Solid	Liquid	Gas	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	Ð	M_p (g mol ⁻¹)
0.4 wt% Ni/CeO ₂ -SA	8	91 (±5)	9 (±5)	82 (±1)	9 (±5)	2949 (±169)	5381 (±416)	1.82 (±0.04)	5997 (±550)
	16	95 (±1)	5 (±1)	78 (±7)	18 (±6)	2530 (±117)	4599 (±150)	1.84 (±0.005)	5090 (±287)
	24	94 (±6)	6 (±6)	76 (±0.2)	18 (±6)	1798 (±75)	3598 (±88)	2.00 (±0.03)	3857 (±37)
	8	85 (±1)	16 (±1)	78 (±2)	6 (±1)	3028 (±163)	5741 (±291)	1.90 (±0.01)	6125 (±463)
0.7 wt% Ni/CeO ₂ -NC	16	96 (±2)	4 (±2)	73 (±5)	24 (±3)	1442 (±109)	2786 (±219)	1.94 (±0.01)	2736 (±273)
	24	93 (±3)	7 (±3)	78 (±6)	15 (±9)	1226 (±84)	2029 (±23)	1.73 (±0.07)	1795 (±197)
1.2 wt% Ni/CeO ₂ -SA	16	89 (±2)	11 (±2)	77 (±1)	12 (±2)	2132 (±55)	4115 (±123)	1.93 (±0.11)	4130 (±160)



Figure S1. GPC chromatograms of liquids produced by **a**) Blank reactions and CeO₂ with PP for 24 h and **b**) Ni/CeO₂ catalysts for various times. Hydrogenolysis reaction conditions: PP (2 g), Ni/CeO₂ (fixed Ni content 0.00138g) or CeO₂ (0.2 g), 280 °C, 30 bar H₂, 500 RPM, 8-24 h. (SA – Sigma Aldrich; NC – nanocube).

Catalyst	Polymer feedstock	Polymer: catalyst	Temperature	H ₂ pressure	Solid polymer deconstruction	Liquid yield	Liquid productivity
		1 200	(°C)	(bar)	(h)	(%)	$(g_{\text{liquid}} g_{\text{Ni}}^{-1} h^{-1})$
5 wt% Ni/SiO2 ¹⁴	PE	5:1	280	30	8	75	9.4ª
15 wt% Ni/SiO ₂ ¹⁵	PE, PP	10:1	300	30	9	65	4.8 ^a
Ni _x Al _y O _z ¹⁶	PE, PP	10:1	300	30	10	74	-
This work: 0.4 wt% Ni/CeO ₂ -SA	РР	5.5:1	280	30	16	78 (±7)	70.9 (±6.3)
This work: 0.7 wt% Ni/CeO ₂ -NC	РР	10:1	280	30	16	73 (±5)	65.9 (±4.5)

Table S3. Comparison of Ni/CeO₂ catalysts to Ni-based catalysts in the literature at complete solid deconstruction. Parenthesises show the standard deviation of multiple reactions. (SA – Sigma Aldrich; NC – nanocube).

(a) Calculated using Equation S3 from reported data.

Table S4. Comparison of liquid productivities,	rate of C-C scission, and $M_{\rm w}$, depolymerisation rate for the	e hydrogenolysis of PP over	r Ni/CeO ₂ catalysts for 24
h.				

Catalyst	Liquid productivity (g _{liquid} g _{Ni} ⁻¹ h ⁻¹)	Average rate of C-C bond scission (mmol g _{Ni} ⁻¹ h ⁻¹)	Average rate of C-C bond scission (with only C ₁ contribution) (mmol g _{Ni} ⁻¹ h ⁻¹)	Average M _w depolymerisation rate (kg mol ⁻¹ g _{Ni} ⁻¹ h ⁻¹)
0.4 wt% Ni/CeO ₂ -SA	46.5	435.5	334.4	253.7
0.7 wt% Ni/CeO2-NC	47.3	576.0	462.6	300.4

Catalyst used	Reaction time (h)	Weight loss in LTO (%)	Weight loss in HTO (%)	Burnout temperature (°C)
	8	96	4	513
0.4 wt% Ni/CeO ₂ -SA	16	98	2	508
	24	98	2	512
1.2 wt% Ni/CeO ₂ -SA	16	98	2	500
	8	95	5	493
0.7 wt% Ni/CeO ₂ -NC	16	96	4	462
	24	97	3	482

Table S5. TGA data of produced liquids in PP hydrogenolysis over Ni/CeO₂ catalysts. Regions: low temperature oxidation (LTO; ca. to 350 °C) and high temperature oxidation (HTO; ca. 450-600 °C), burnout temperature is the temperature at which complete oxidation of liquid occurs.



Figure S2. TGA of the oxidation profile of produced liquids in PP hydrogenolysis over Ni/CeO₂ catalysts after (a) 8 h and (b) 24 h.



Figure S3. STEM-HAADF and corresponding BF images from multiple sample locations and magnifications of fresh 0.4 wt% Ni/CeO₂-SA.



Figure S4. STEM-HAADF and corresponding BF images from multiple sample locations and magnifications of fresh 0.7 wt% Ni/CeO₂-NC.



Figure S5. STEM-HAADF and corresponding BF images from multiple sample locations and magnifications of post 16 h reaction 0.4 wt% Ni/CeO₂-SA.



Figure S6. STEM-HAADF and corresponding BF images from multiple sample locations and magnifications of post 16 h reaction 0.7 wt% Ni/CeO₂-NC.



Figure S7. Linear combination fitting of Ni K-edge XANES of fresh 0.4 wt% Ni/CeO₂-SA and 0.7 wt% Ni/CeO₂-NC



Figure S8. Linear combination fitting of Ni K-edge XANES of post 16 h reaction 0.4 wt% Ni/CeO₂-SA and 0.7 wt% Ni/CeO₂-NC



Figure S9. a) *R*-space, **b)** *k*-space, **c)** *q*-space of the Ni K-edge EXAFS fitting and k^2 weighted data for a crystalline NiO standard. Fits were conducted using a two-shell model with single scattering Ni-O and Ni-Ni paths in the range: $3 < k < 10 \text{ Å}^{-1}$, 1.0 < R < 3.3 Å.



Figure S10. a) *R*-space, b) *k*-space, c) *q*-space of the Ni K-edge EXAFS fitting and k^2 weighted data for a Ni(0) foil standard. Fits were conducted using a single-shell model of single scattering Ni-Ni paths in the range: $3 \le k \le 10$ Å⁻¹, $1.0 \le R \le 3.3$ Å.



Figure S11. Morlett wavelet transformations of k^2 weighted data from Ni K-edge EXAFS spectra of a crystalline NiO standard. The wavelet transformation of NiO shows a feature at ΔR 1-2 Å and Δk 3-6 Å⁻¹ associated with the 1st shell Ni-O₆, and a more intense feature at ΔR 2-3 Å and Δk 5-9 Å⁻¹ which is attributed to the 2nd shell single scattering Ni-Ni path and associated multiple scattering paths.



Figure S12. Morlett wavelet transformations of k^2 weighted data from Ni K-edge EXAFS spectra of a Ni(0) foil standard. The wavelet transformation of Ni(0) foil shows a strong feature at ΔR 1.5-3 Å and Δk 4-10 Å⁻¹, which includes the dominant single scattering Ni-Ni(2) path and multiple scattering paths.



Figure S13. a) *k*-space and **b)** *q*-space of the Ni K-edge EXAFS fitting and k² weighted data for fresh 0.4 wt% Ni/CeO₂-SA. Fits were conducted using a two-shell model with single scattering Ni-O and Ni-Ni(1) paths associated with NiO in the range: $3 \le k \le 10 \text{ Å}^{-1}$, $1.0 \le R \le 3.3 \text{ Å}$.



Figure S14. a) *k*-space and **b)** *q*-space of the Ni K-edge EXAFS fitting and k² weighted data for fresh 0.7 wt% Ni/CeO₂-NC. Fits were conducted using a two-shell model with single scattering Ni-O and Ni-Ni(1) paths associated with NiO in the range: $3 \le k \le 10 \text{ Å}^{-1}$, $1.0 \le R \le 3.3 \text{ Å}$.



Figure S15. a) *k*-space and b) *q*-space of the Ni K-edge EXAFS fitting and k^2 weighted data for post 16 h reaction and exposure to air 0.4 wt% Ni/CeO₂-SA. Fits were conducted using a two-shell model with single scattering Ni-O and Ni-Ni(1) paths associated with NiO and single scattering Ni-Ni(2) path associated with Ni(0) in the range: 3 < k < 10 Å⁻¹, 1.0 < R < 3.3 Å.



Figure S16. a) *k*-space and **b)** *q*-space of the Ni K-edge EXAFS fitting and k² weighted data for post 16 h reaction and exposure to air 0.7 wt% Ni/CeO₂-NC. Fits were conducted using a two-shell model with single scattering Ni-O and Ni-Ni(1) paths associated with NiO and single scattering Ni-Ni(2) path associated with Ni(0) in the range: 3 < k < 10 Å⁻¹, 1.0 < R < 3.3 Å.



Figure S17. N₂ adsorption-desorption isotherms for a) CeO₂-SA and b) CeO₂-NC.



Figure S18. GPC chromatograms of liquids produced by Ni/CeO₂ catalysts with various Ni densities after 16 h. Hydrogenolysis reaction conditions: PP (2 g), Ni/CeO₂ (fixed Ni content 0.00138g), 280 °C, 30 bar H₂, 500 RPM, 16 h. (SA – Sigma Aldrich; NC – nanocube).



Figure S19. TGA of the oxidation profile of produced liquids in PP hydrogenolysis over Ni/CeO_2 catalysts with various Ni densities after 16 h. (SA – Sigma Aldrich; NC – nanocube).

Table S6. Liquid productivities, rate of C-C scission, and M_w depolymerisation rate for the hydrogenolysis of PP over 1.2 wt% Ni/CeO₂-SA for 16 h. (SA – Sigma Aldrich; NC – nanocube).

Catalyst	Liquid productivity (g _{liquid} g _{Ni} ⁻¹ h ⁻¹)	Average rate of C-C bond scission (with only C ₁ contribution) (mmol g _{Ni} ⁻¹ h ⁻¹)	Average <i>M</i> _w depolymerisation rate (kg mol ⁻¹ g _{Ni} ⁻¹ h ⁻¹)
1.2 wt% Ni/CeO ₂ -SA	69.7	365.0	357.1
0.4 wt% Ni/CeO ₂ -SA	70.9	353.5	335.2



Figure S20. STEM-HAADF images of **a**) fresh 0.4 wt% Ni/CeO₂-SA and **b**) 0.4 wt% Ni/CeO₂-SA post 16 h reaction, and its corresponding FFT and inversed FFT by applying a mask in the (111) planes (indicated by blue arrows). The planes highlighted are the corresponding facet and further indicated with the blue arrows. Measured interplanar spacing for the surface facet of both samples was 0.313 nm, which corresponds to the d-spacing of the (111) plane.



Figure S21. STEM-HAADF images of **a**) fresh 0.7 wt% Ni/CeO₂-NC and **b**) 0.7 wt% Ni/CeO₂-NC post 16 h reaction, and its corresponding FFT and inversed FFT by applying a mask in the (200) planes (indicated by blue arrows). The planes highlighted are the corresponding facet and further indicated with the blue arrows. Measured interplanar spacing for the surface facet of both samples was 0.270 nm, which corresponds to the d-spacing of the (200) plane, which confirms the nanocubes are enclosed by the iso-structural (100) plane.

Catalyst	Lattice parameters ^a (Å)	Cell volume ^a (Å ³)	CeO2 Scherrer crystallite size (nm)
0.4 wt% Ni/CeO ₂ -SA fresh	5.42384(5)	159.559(3)	29.6 (±1.2)
0.4 wt% Ni/CeO2-SA 8 h reduced	5.42567(3)	159.632(3)	29.3 (±1.2)
0.4 wt% Ni/CeO2-SA post 16 h reaction	5.424840(9)	159.647(1)	29.9 (±1.2)
0.7 wt% Ni/CeO2-NC fresh	5.42585(3)	159.736(3)	23.8 (±1.6)
0.7 wt% Ni/CeO2-NC 8 h reduced	5.42942(2)	160.052(1)	24.4 (±1.6)
0.7 wt% Ni/CeO2-NC post 16 h reaction	5.42693(3)	159.832(2)	24.8 (±1.5)

Table S7. Calculated lattice parameters, cell volume, and CeO₂ crystallite size of fresh, reduced, and post reaction Ni/CeO₂ catalysts from synchrotron PXRD data. (SA – Sigma Aldrich; NC – nanocube).

^a cubic unit cell parameters: a = b = c and calculated through Pawley fitting of the XRD patterns.



Figure S22. Pawley refinement of synchrotron PXRD data measured at I11 beamline ($\lambda = 0.825479$ Å) of **a**) 0.4 wt% Ni/CeO₂-SA fresh, **b**) 0.7 wt% Ni/CeO₂-NC fresh, **c**) 0.4 wt% Ni/CeO₂-SA post 16 h reaction, and **d**) 0.7 wt% Ni/CeO₂-SA post 16 h reaction. (SA – Sigma Aldrich; NC – nanocube).

Catalyst	Miller	d-spacing	2Theta	FWHM
	Indices (hkl)	(nm)		
	(111)	0.312	15.2	0.186
0.4 with Ni/CoO. SA fresh	(200)	0.271	17.5	0.166
$0.4 \text{ wt/} / 10 \text{ NI/CeO}_2 - SA Hesh$	(220)	0.191	24.9	0.187
	(311)	0.163	29.3	0.195
	(111)	0.312	15.2	0.176
0 4 with Ni/Coo SA post 16 h monstion	(200)	0.271	17.5	0.163
$0.4 \text{ wt\% NI/CeO}_2$ -SA post 16 h reaction	(220)	0.191	24.9	0.179
	(311)	0.163	29.3	0.187
	(111)	0.312	15.2	0.139
0.7 mill Ni/C-O NC funct	(200)	0.271	17.6	0.161
$0.7 \text{ wt% m/CeO}_2\text{-nC fresh}$	(220)	0.191	24.9	0.147
	(311)	0.163	29.3	0.153
	(111)	0.312	15.2	0.138
0.7 mill NilCaO NC mart 16 h manting	(200)	0.271	17.5	0.160
0.7 wt% m/CeO ₂ -mC post 16 h reaction	(220)	0.191	24.9	0.146
	(311)	0.163	29.3	0.152

Table S8. Full width half maximum (FWHM) of characteristic CeO₂ diffraction peaks from I11 synchrotron powder data ($\lambda = 0.825479$ Å) with 2Theta, d spacing, and miller indices of fresh and post 16 h reaction catalysts.

XPS	Scan region	0.4 wt% Ni/CeO ₂ - SA fresh	0.4 wt% Ni/CeO2- SA reduced 8 h	0.4 wt% Ni/CeO ₂ - SA post 16 h reaction	0.7 wt% Ni/CeO ₂ - NC fresh	0.7 wt% Ni/CeO2-NC reduced 8 h	0.7 wt% Ni/CeO2-NC post 16 h reaction
Ce 3d	Component/peak	881.0 (Ce(III) v ⁰)	880.8 (Ce(III) v ⁰)	880.6 (Ce(III) v ⁰)	880.8 (Ce(III) v ⁰)	880.8 (Ce(III) v ⁰)	880.9 (Ce(III) v ⁰)
	binding energy (eV)	885.6 (Ce(III) v ^I)	884.7 (Ce(III) v ^I)	885.0 (Ce(III) v ^I)	885.8 (Ce(III) v ^I)	884.5 (Ce(III) v ^I)	885.2 (Ce(III) v ^I)
		898.0 (Ce(III) u ⁰)	898.3 (Ce(III) u ⁰)	898.6 (Ce(III) u ⁰)	898.8 (Ce(III) u ⁰)	898.4 (Ce(III) u ⁰)	898.5 (Ce(III) u ⁰)
		903.2 (Ce(III) u ^I)	903.0 (Ce(III) u ^I)	903.6 (Ce(III) u ^I)	903.2 (Ce(III) u ^I)	903.4 (Ce(III) u ^I)	903.2 (Ce(III) u ^I)
		882.5 (Ce(IV) v)	882.2 (Ce(IV) v)	882.4 (Ce(IV) v)	882.5 (Ce(IV) v)	881.9 (Ce(IV) v)	882.4 (Ce(IV) v)
		888.9 (Ce(IV) v ^{II})	888.6 (Ce(IV) v ^{II})	888.8 (Ce(IV) v ^{II})	888.8 (Ce(IV) v ^{II})	888.3 (Ce(IV) v ^{II})	888.7 (Ce(IV) v ^{II})
		898.5 (Ce(IV) v ^{III})	898.1 (Ce(IV) v ^{III})	898.2 (Ce(IV) v ^{III})	898.1 (Ce(IV) v ^{III})	897.7 (Ce(IV) v ^{III})	898.1 (Ce(IV) v ^{III})
		901.1 (Ce(IV) u)	900.8 (Ce(IV) u)	901.0 (Ce(IV) u)	901.0 (Ce(IV) u)	900.5 (Ce(IV) u)	900.8 (Ce(IV) u)
		907.5 (Ce(IV) u ^{II})	907.2 (Ce(IV) u ^{II})	907.6 (Ce(IV) u ^{II})	907.5 (Ce(IV) u ^{II})	907.0 (Ce(IV) u ^{II})	907.5 (Ce(IV) u ^{II})
		916.6 (Ce(IV) u ^{III})	916.3 (Ce(IV) u ^{III})	916.6 (Ce(IV) u ^{III})	916.4 (Ce(IV) u ^{III})	916.1 (Ce(IV) u ^{III})	916.5 (Ce(IV) u ^{III})
	Atom%	19.8	18.8	16.5	16.6	14.0	15.4
Ni 2p	Component/peak binding energy (eV)	885.6	854.9	885.4	885.8	854.8	885.6
	Atom%	0.8	1.2	0.8	1.1	1.4	1.2
O 1s	Component/peak	529.4 (M-O)	529.3 (M-O)	529.3 (M-O)	529.2 (M-O)	528.9 (M-O)	529.2 (M-O)
	binding energy (eV)	531.4 (M-OH/	530.9 (M-OH/	530.7 (M-OH/	531.3 (M-OH/	530.4 (M-OH/	530.7 (M-OH/
		M-CO ₃)	M-CO ₃)	M-CO ₃)	M-CO ₃)	M-CO ₃)	M-CO ₃)
		532.2 (O _{ads})	532.0 (O _{ads})	532.1 (O _{ads})	532.4 (O _{ads})	531.8 (O _{ads})	532.1 (O _{ads})
	Atom%	49.7	48.7	46.9	50.7	45.1	47.2
C 1s + Ce 4s	Component/peak	284.8 (C-C/C-H)	284.8 (C-C/C-H)	284.8 (C-C/C-H)	284.7 (C-C/C-H)	284.8 (C-C/C-H)	284.8 (C-C/C-H)
	binding energy (eV)	286.6 (C-O)	285.9 (C-O)	286.0 (C-O)	286.7 (C-O)	286.3 (C-O)	286.0 (C-O)
		288.6 (C=O)	288.9 (C=O)	288.9 (C=O)	288.7 (C=O)	288.6 (C=O)	288.9 (C=O)
		290.0 (Ce 4s)	290.0 (Ce 4s)	289.9 (Ce 4s)	290.2 (Ce 4s)	289.4 (Ce 4s)	289.4 (Ce 4s)
	Atom%	29.8	31.3	35.9	31.6	39.5	36.2

Table S9. XPS analysis surface data for Ce 3d, Ni 2p, C 1s, Ce 4s, and O 1s for fresh, reduced 8 h, and post reaction catalysts. Reduced catalysts were analysed after inert transfer.



Figure S23. TPR data of CeO₂-SA with Lorentzian peak fitting after background correction.



Figure S24. TPR data of CeO₂-NC with Lorentzian peak fitting after background correction.

Material	Ni reduction peak temperatures	Ni uptake	CeO2 surface peak temperatures ^b	CeO2 surface H2 uptake	CeO2 bulk peak temperature ^b	CeO2 bulk H2 uptake
		(µmol)	(°C)	(µmolg ⁻¹)	(°C)	(µmolg ⁻¹)
CeO ₂ -SA	-	-	358, 415	92	734	788
CeO ₂ -NC	-	-	412, 506	430	712	710
Ni/CeO ₂ -SA	231, 283	13	325	38	731	850
Ni/CeO ₂ -NC	228, 310	12	349	240	724	591

Table S10. TPR uptake data for supports (CeO₂-SA and CeO₂-NC) and catalysts (Ni/CeO₂-SA and Ni/CeO₂-NC) from fitted profiles.



Figure S25. Synchrotron PXRD patterns of reduced catalysts following inert transfer and torch sealing under inert atmosphere.



Figure S26. TCD signal of 5% H_2 /Ar reduction treatment of CeO₂-SA prior to dosing with probe molecules (CO₂/NH₃) for TPD analysis. Samples were reduced at 550 °C for 30 min and cooled under flow to yield surface reduced CeO₂.



Figure S27. TCD signal of 5% H_2/Ar reduction treatment of CeO₂-NC prior to dosing with probe molecules (CO₂/NH₃) for TPD analysis. Samples were reduced at 550 °C for 30 min and cooled under flow to yield surface reduced CeO₂.



Figure S28. Temperature programmed desorption profile of adsorbed NH₃ over fresh and surface reduced CeO₂ supports.



Figure S29. Temperature programmed desorption profile of adsorbed CO_2 over fresh and surface reduced CeO_2 supports.

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