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# Enhanced production and control of liquid alkanes in the hydrogenolysis of polypropylene over shaped Ru/CeO<sub>2</sub> catalysts

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#### ABSTRACT

The hydrogenolysis of polypropylene waste to liquid hydrocarbons offers a promising pathway for the chemical recycling of waste polymers. This work describes the importance of reaction conditions and support morphology to produce high liquid yields with enhanced control of chain length over highly active shaped and non-shaped Ru/CeO<sub>2</sub> catalysts. The shaped 2 wt% Ru/CeO<sub>2</sub> exhibit high liquid alkane yields (58–81%) when compared to the non-shaped 2 wt% Ru/CeO<sub>2</sub> (liquid yield: 34–58%) under optimized reaction conditions (220 °C, 16 h, 30 bar H<sub>2</sub>). In particular, the 2 wt% Ru/CeO<sub>2</sub> nanocube catalyst exhibits the highest activity yielding lighter hydrocarbons. This was rationalized to be a combination of small Ru cluster formation and enhanced metal-support interactions. The influence of larger Ru particles ( $\geq$ 1.5 nm) was confirmed mechanistically using a computational density functional theory study on the hydrogenolysis of pentane (C<sub>5</sub>) to determine the favorable formation of methane in the non-shaped Ru/CeO<sub>2</sub> catalyst.

#### 1. Introduction

The large-scale production and consumption of olefin plastics such as polyethylene (PE) and polypropylene (PP) is generating significant amounts of nondegradable plastic waste, resulting in severe environmental consequences. Currently, plastic waste is buried in landfill (70%), mechanically recycled (16%), and incinerated (14%) [1–6]. Mechanical recycling and incineration often result in low-quality products and considerable energy loss [2,7]. Other recycling methods such as thermo-chemical methods which include pyrolysis, catalytic cracking, and olefin-mediated metathesis enable polyolefin depolymerization to chemicals [8–13]. However, these processes also suffer from a high energy demand and poor product selectivity.

A promising route to plastic waste upcycling is the catalytic hydrogenolysis process, which utilises catalysts to promote C-C bond scission at mild operating conditions ( $\leq$  300 °C), with a larger degree of control over product selectivity [2,6,14–17]. The selective production of high-value liquid alkanes from waste is essential to move towards a circular economy [18,19]. Ruthenium is considered to have high

activity for the hydrogenolysis of polymers [20]. Although the formation of undesired low-value products (gases or waxes) through cleavage of the terminal C-C bond is common [21]. However, the regioselectivity of the hydrogenolysis reaction is governed by Ru particle size with sub-nanometer species facilitating cleavage of internal C-C bonds reducing methane production [22]. Furthermore, single atom Ru/CeO<sub>2</sub> catalysts have been shown to effectively supress terminal cleavage to form methane [23]. The activity and selectivity of catalysts is also affected by the nature of the feedstock, with the chemical upcycling of PE exploited extensively [24-31]. PP hydrogenolysis is more challenging due to the Ctertiary-Csecondary bonds present in highly branched PP being less susceptible to hydrogenolysis than the predominant Csecondary-Csecondary bonds in PE [32,33]. The tacticity and molecular weight of PP has also been shown to have a large effect on the polydispersity of the final liquid product [34]. Therefore, achieving high selectivity to light liquid hydrocarbons remains challenging [22,33,35–37]. Enhanced design of highly active heterogeneous catalysts and optimised process conditions are needed to enable the selective transformation of polyolefins to liquid products with a narrow molecular distribution while

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reducing yields to gas or wax products. Additionally, enhanced control of the produced alkane chain lengths could increase the potential applications of the liquid products to include repolymerisation, lubricants, chemicals, or fuels.

Particle engineering to achieve controlled shapes such as nanocubes or nanorods leads to enhanced control of the surface termination or facet [38–40]. In particular, shaped CeO<sub>2</sub> particles prepared by hydrothermal methods, used either as a support or catalyst, have shown enhanced catalytic activity and selectivity in various catalytic reactions [41-44]. CeO2 nanocubes are enclosed by six {100} faces and frequently show rounded corners and edges exposing {111} and {110} surfaces [44]. Whereas, CeO<sub>2</sub> nanorods are commonly reported to expose {110} and {100} planes, however, restructuring of these surfaces occur, leading to the generation of {111} exposed facets with structural defects [45-47]. These well-defined exposed facets on shaped CeO<sub>2</sub> particles have also been shown to enhance metal-support interaction, with the formation of highly dispersed Ru species on nanorods and nanocubes [48-51]. Shaped catalysts with controlled facets have been reported for plastic hydrogenolysis, with SrTiO<sub>3</sub> nanocubes controlling the electronic and geometric properties of Pt nanoparticles deposited by atomic laver deposition or organometallic grafting [52-54]. This led to enhanced activity in PE and PP hydrogenolysis at 300 °C, with a high selectivity to light hydrocarbons. CeO<sub>2</sub> nanorods have also been shown to adjust the electronic properties of Ru to increase yield to liquid products through improved internal cleavage [55]. These studies demonstrate the applicability of shaped catalysts for the hydrogenolysis of waste plastics.

Motivated by the widespread applications of shaped nanomaterials and high liquid yields obtained over Ru/CeO2 catalysts, herein we report the use of shaped CeO<sub>2</sub> (nanorods and nanocubes) as supports for Ru species, with non-shaped Ru/CeO2 catalysts also synthesised for comparison. The catalysts were assessed in hydrogenolysis reactions of various pristine and post-consumer polypropylene (PP). An investigation of the effect of reaction conditions (temperature, H<sub>2</sub> pressure, time) on liquid yields and the tuneability of the composition of the liquid product was conducted. The product distribution was correlated with the physicochemical properties of the shaped catalysts to elucidate their role in controlling the selectivity of products towards liquid hydrocarbons. Finally, a theoretical investigation, using quantum chemical approaches based on density functional theory (DFT), of the hydrogenolysis of pentane on Ru(0001) surface was undertaken to elucidate the role of larger Ru particles in determining the regioselectivity of the reaction and the consequent production of methane. Although pentane is a small hydrocarbon, it includes the regioselectivity aspects, provides the same building block of -CH<sub>2</sub> as polymer polypropylene, and represents propylene branching through the terminal methyl group. Moreover, pentane is thermodynamically more stable than its longer homologues and does not undergo direct aromatization [56].

#### 2. Experimental

#### 2.1. Materials

CeO<sub>2</sub> (nanopowder, <25 nm) was procured from Sigma Aldrich and was used as catalyst support (CeO<sub>2</sub>-SA) without any pre-treatment. Metal precursors Ce(NO<sub>3</sub>)<sub>3</sub>.6 H<sub>2</sub>O (>99%) and ruthenium (III) nitrosyl nitrate (Ru 31.3%) were obtained from Sigma Aldrich while the structure directing agent NaOH (99.99%) used for the synthesis of shaped CeO<sub>2</sub> was obtained from Fisher Scientific UK. The bulk RuO<sub>2</sub> (99.99% metal basis) and biphenyl (internal standard) were also procured from Sigma Aldrich. Anhydrous ethanol (>99.5%) and dichloromethane ( $\geq$ 99.8%) solvents used in the synthesis of materials and reaction product analysis were purchased from Sigma Aldrich. The standard calibration gases (C<sub>1</sub>-C<sub>5</sub>) were purchased from BOC UK. Isotactic polypropylene (i-PP-12 K and i-PP-250 K) of two different weight average molecular weights (M<sub>w</sub> ~12,000 Da and 250,000 Da) were procured

from Sigma Aldrich. All materials were used as received without further purification. Post-consumer polypropylene plastics such as centrifuge tube (PP-CT), file sheet (PP-FS) and fragrance case (PP-FC) were collected from the laboratory, office, and supermarket respectively, and were washed under hot water and dried in the air followed by chopping into uniform sizes of 10–15 mm. Images and vendor information for the post-consumer plastics are given in the supporting information.

#### 2.2. Catalyst preparation

#### 2.2.1. Preparation of shaped CeO<sub>2</sub> supports

CeO<sub>2</sub> nanocube and nanorod shaped supports were synthesized by a hydrothermal method following the literature [42]. In general, 0.868 g of Ce(NO<sub>3</sub>)<sub>3</sub>.6 H<sub>2</sub>O was dissolved in 6 M aqueous NaOH solution (35 mL) in a 125 mL Teflon cup and stirred for 30 min. The resulting purple milky suspension was transferred into a stainless-steel autoclave and subjected to different thermal treatments. CeO<sub>2</sub> nanorods were prepared at 100 °C for 24 h while the CeO<sub>2</sub> nanocubes were obtained at 180 °C for 24 h. The precipitate was washed with deionized water and ethanol and dried in an oven at 110 °C for 12 h. The dried product was calcined in a muffle furnace at 500 °C for 4 h. The as-synthesized CeO<sub>2</sub> were named CeO<sub>2</sub>-NR and CeO<sub>2</sub>-NC where NR and NC stand for nanorods and nano-cubes respectively.

#### 2.2.2. Impregnation of Ru nanoparticles

A series of shaped (CeO2-NR and CeO2-NC) and commercial (CeO2-SA) CeO<sub>2</sub> based catalysts with Ru loading in the range (0.5–5 wt%) were synthesized by an incipient wetness impregnation method using ruthenium nitrosyl nitrate (31.3% Ru) as the metal precursor. Briefly, depending upon the Ru loading, a known amount of Ru salt is dissolved in a known volume of de-ionized water calculated from the pore volume and the weight of CeO2. For example, in the synthesis of 2 wt% Ru/ CeO2-NR catalyst, 0.1955 g of Ru salt is dissolved in 1 mL of deionized water and the solution is impregnated on 3 g of CeO2-NR oxide under constant stirring. The impregnated solid was then dried overnight in an oven at 110 °C and calcined in a furnace at 500 °C for 4 h using a heating rate of 5 °C min<sup>-1</sup> under static air. All the catalysts were reduced prior to the hydrogenolysis experiments at 300 °C for 2 h at 10 °C min<sup>-1</sup> under 10% H<sub>2</sub>/Ar. The synthesized catalysts were named xRu/CeO<sub>2</sub>-SA/NR/ NC, where x denotes the ruthenium loading in wt% and SA stands for oxides obtained from Sigma Aldrich, NR for nanorods, NC for nanocubes.

#### 2.3. Catalyst characterization

### 2.3.1. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis

The bulk metal composition of the calcined catalysts was measured using an Agilent 5110 ICP-OES instrument. Samples for ICP analysis were prepared by dissolving a ground sample (50 mg) in 10 mL concentrated hydrochloric acid (37%) and heated in a 15 mL Teflon-coated acid-digestor to 220  $^{\circ}$ C for 12 h. The mixture was further diluted to 50 mL using ultra-pure water before ICP-OES analysis. Ru and Ce elements were analysed with all analyses performed in triplicate.

#### 2.3.2. Porosimetry analysis

 $\rm N_2$  adsorption/desorption isotherms were measured at - 196 °C using a Micromeritics Tristar II. Prior to the measurements, samples were degassed overnight at 110 °C. The specific area was calculated using the Brunauer-Emmett-Teller (BET) equation in the  $P/P_0$  range 0.05–0.3, while the pore size distribution was obtained from the desorption branch using the Barrett-Joyner-Halenda (BJH) method.

#### 2.3.3. PXRD analysis

Powder X-ray diffraction (PXRD) patterns were recorded on a Panalytical X'Pert Pro diffractometer with Co  $K_{\alpha 1}$  radiation ( $\lambda = 1.7890$  Å).

The patterns were collected over the range  $10^{\circ} < 2\theta < 100^{\circ}$  with a step size of  $0.017^{\circ}$  s<sup>-1</sup>. The phase identification was performed using the Joint Committee on Powder Diffraction (JCPDS) database and the X'Pert HighScore Plus software. The mean metal crystallite size was calculated from the line broadening using the Scherrer equation.

#### 2.3.4. H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR)

Reduction profiles of the calcined samples were measured using a Micromeritics AutoChem 2920 instrument with a thermal conductivity detector (TCD) and a cold trap before the detector. The profiles were recorded by reducing ca. 50 mg of the sample under 5%  $H_2/N_2$  flow (50 mL min<sup>-1</sup>) and heating the sample from 30 °C to 800 °C using a ramp rate of 10 °C min<sup>-1</sup>.

#### 2.3.5. CO pulse chemisorption

Pulse CO chemisorption measurements were performed on a Micromeritics AutoChem 2920 instrument. Briefly, a known amount of sample (ca. 60 mg) was pre-reduced under 5%H<sub>2</sub>/N<sub>2</sub> (50 mL min<sup>-1</sup>) at 300 °C for 30 min using a ramp rate of 10 °C min<sup>-1</sup>. The sample was cooled to 40 °C and CO chemisorption analysis was performed by introducing successive pulses of 10% CO/He. The pulses were repeated until no further change in the peak area were noted. The amount of CO uptake afforded the measurement of the metal dispersion (%D), metal surface area per gram of metal (Am), and the average particle size of metal (Sm). The stoichiometry factor (S.F.) between Ru metal atoms and CO molecules was assumed to be 1 [57].

#### 2.3.6. TEM and HAADF-STEM-EDX

Transmission electron microscopy (TEM) images were obtained with a JEOL 2100 + microscope operating at 200 KV. High angle annular dark field (HAADF), bright field (BF) scanning transmission electron microscopy (STEM) imaging were performed using Cs-corrected TEM/ STEM JEOL 2100FCs microscope operating at 200 KV. For STEM-EDX mapping, a JEOL EDX Silicon drift detectors (SDD) were used with a detection area of 100 nm<sup>2</sup>. Samples were prepared by dispersion in acetone and deposition on a carbon-coated Cu grid.

#### 2.3.7 XPS analysis

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo NEXSA XPS fitted with a monochromated Al k $\alpha$  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  $\mu$ 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 the high-resolution scans of Ce 3d, C 1 s/Ru 3d/Ce 4 s, and O 1 s. No other major species were noted in the survey scans. The RuO<sub>2</sub> and Ce<sup>3+</sup> components were calculated as a percentage of their total components using the following equations:

$$RuO_2(\%) = 100 \times \left(\frac{[RuO_2]}{[RuO_2] + [Ru(0)]}\right)$$
(1)

$$Ce^{3+}(\%) = 100 \times \left(\frac{[Ce^{3+}]}{[Ce^{3+}] + [Ce^{4+}]}\right)$$
(2)

#### 2.4. Catalytic testing

Catalytic hydrogenolysis of polymers were carried out using a Parr 4590 series reactor (100 mL) equipped with a glass liner and a Parr 4848 reactor control system. In the catalytic hydrogenolysis of polymers, 2 g of polymer and 0.1 g of pre-reduced catalyst was loaded into the autoclave. The reactor was then sealed and flushed with N<sub>2</sub> and H<sub>2</sub> respectively, followed by pressurizing the reactor to the required H<sub>2</sub> pressure (10-30 bar). The reaction was carried out at various temperatures (180-250 °C) and times (8-60 h) with a 500 RPM stirring rate. After cooling the reactor to room temperature, the gases from the headspace were analyzed by an online Agilent 8860 GC using CP-Sil 8 CB column (50 m X 0.32 mm $\times$ 5 µm) equipped with an FID detector. The gas concentration was calculated by using a standard C1-C5 calibration gas mixture. After the gas analysis, the remaining gas was vented, and 30 mL of dichloromethane (DCM) was used to solvate the liquid products in the autoclave. The slurry was stirred and filtered with the solid residue was left to dry at ambient temperature overnight. The liquid fraction was concentrated over the rotary evaporator to remove the solvent.

The average molecular weight distribution and polydispersity index of liquid products were estimated using gel permeation chromatography (GPC) on a Viscotek TDA302 GPC (THF) instrument equipped with T600, T2500, and T6000 columns in series and refractive index (RI) detector. Tetrahydrofuran (THF) was used as a mobile phase with 1 mL min<sup>-1</sup> flow, and an injection volume of 100  $\mu$ L. Column and detector temperature was kept at 35 °C. Calibrations curves of mixed polystyrene standards were used for quantification of weight average molecular weight (M<sub>w</sub>), number average molecular weight (M<sub>n</sub>), and polydispersity index (PDI) of different polymers and reaction products. The solid and liquid fractions were weighed for the quantification. The solid conversion, percentage yield of individual collected fractions (solid, liquid, and gas), percentage depolymerization (DP), and reaction rates, were obtained as per the following equations:

Solid Conversion (%) = 
$$\left(\frac{\left(\left(\max s \ polymer_{in} \left(g\right) - \max s \ solid \ recovered \left(g\right)\right) - \max s \ cat(g)\right)}{\max s \ polymer_{in} \left(g\right)}\right) \times 100$$
 (3)

using a Dual-beam low-energy electron/ion source (Thermo Scientific FG-03). Ion gun current = 150  $\mu$ 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. 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 or asymmetric line shapes were used to fit Ce(IV) (LA(0.9,2,50), Ru(0) (3d<sub>5/2</sub> - LF (0.8,2.34,500,180) and 3d<sub>3/2</sub> – (LF(1.01,1.24,500,50)), and RuO<sub>2</sub> components (LF(0.25, 1, 45, 280)). Atomic percentages were calculated

$$Yield (\%) = \left(\frac{mass \ of \ each \ product(g)}{mass \ polymer_{in}(g)}\right) \times 100$$
(4)

$$DP(\%) = \left(\frac{(M_w \ polymer_{in} - M_w \ liquid \ product)}{M_w \ polymer_{in}}\right) \times 100$$
(5)

Reaction rate 
$$(g_{pp\ depoly}.h^{-1}.g_{metal}^{-1}) = \left(\frac{(mass\ polymer_{in}\ (g) \times DP\ (\%))}{(Time(h) \times Mass\ Ru(g) \times 100)}\right)$$
  
(6)

#### 2.5. Models and computational methods

A systematic computational investigation of pentane  $(C_5H_{12})$ hydrogenolysis on Ru(0001) surfaces was carried out using periodic quantum-chemical calculations as implemented in VASP [58-60]. The considered method RPBE-D3 includes the generalized gradient approximation (GGA) based revised Perdew-Burke-Ernzerhof (PBE) [61,62]. with long-range dispersion corrections including zero-damping function [63,64]. We have tested other functionals ranging from PBE to PBESol and RPBE with and without dispersion corrections including D3 (with Becke-Johnson damping function) and D4. According to our test calculations (see Table S12), the cohesive energy and lattice parameters are well converged with the considered RPBE-D3 functional. The other functionals provide similar trends of the calculated properties as also observed in previous investigations [65–68]. The core electrons for Ru, C and H were defined by standard sets of pseudopotentials (PPs) within the projector-augmented wave (PAW) method [69]. With plane-wave methods, the quality of the basis set is determined by a single parameter, the energy cutoff  $E_{cut}$ . We have used a converged value of  $E_{cut}$ = 520 eV. The integration in reciprocal space was performed with a Monkhorst–Pack grid [70]. The *k*-points grids were augmented for the bulk Ru where converged value of  $11 \times 11 \times 6$  was achieved at  $10^{-6}$  eV per cell. The convergence of the calculated properties with respect to  $E_{\rm cut}$  and *k*-points grids are provided in supporting info (Figs. S13 and S14).

Recent computational and experimental studies have predicted that (0001) surface is the most stable surface plane of the hcp metal Ru [68, 71,72]. Therefore, based on the optimized bulk structures, slabs of Ru (0001) were modeled with increasing number of layers. This simplistic model will describe the activity of main NP facets with little influence from low coordinated atoms and support i.e, medium and large Ru particles. The convergence of total energy as a function of the number of layers was verified by calculating the surface energy  $\gamma$  (the difference in the total energy between the bulk and the surface per formula unit) with Eq. 7:

$$\gamma = \frac{E_{Slab} - m E_{Bulk}}{2A} \tag{7}$$

where  $E_{Slab}$  is the total energy of the two-dimensional slab containing mformula units of metal,  $E_{Bulk}$  is the total energy per bulk metal, and A is the surface area of the slab. The factor 2 in this equation implies that the slab has two identical surfaces, top and bottom. Our calculated converged value of surface energy of Ru(0001) is  $3.33 \text{ J/m}^2$ , which is in well agreement with the previous calculated  $(2.33-3.13 \text{ J/m}^2 \text{ [68]})$  and  $3.35 \text{ J/m}^2$  [71]) and experimental (3.04 J/m<sup>2</sup>) values [72]. A converged 6 layer slab with  $p(4 \times 4)$  supercell size (dimensions: 10.794 Å x 10.794 Å x 27.82 Å) was employed where the top three layers were relaxed and the bottom three layers were kept frozen at the bulk optimized lattice. A vacuum layer of 20 Å along the z direction perpendicular to the surface (the x and y surface directions) was employed to prevent spurious interactions between the repeated slabs. A converged value of  $(3 \times 3 \times 1)$  Monkhorst-Pack grid was used for the *k*-space sampling. The reaction energy of each elementary step along the hydrogenolysis ( $\Delta E$ ) was calculated as the difference between the total energy of the system  $(E_{sys})$  and the combined reference energy of the bare Ru(0001) surface ( $E_{Slab}$ ), the isolated pentane ( $E_{C5}$ ), and hydrogen molecules  $(E_{H2})$  as in Eq. 8, where n is the number of hydrogens considered.

$$\Delta E = E_{sys} - (E_{Slab} + E_{C_5} + \frac{n}{2}E_{H_2})$$
(8)

Table 1

Structure and physiochemical properties of  $2\mathrm{Ru}/\mathrm{CeO}_2$  catalysts and  $\mathrm{CeO}_2$  supports.

Catalyst	Measured Ru content (wt%) <sup>a</sup>	Surface area (m²/g) <sup>b</sup>	CeO <sub>2</sub> crystallite size (nm) <sup>c</sup>			
CeO <sub>2</sub> -SA	-	41	21			
CeO2-NR	-	98	8			
CeO2-NC	-	35	20			
2Ru/CeO2-SA	1.94	40	20			
2Ru/CeO2-NR	1.40	84	8			
2Ru/CeO2-NC	1.74	25	22			

<sup>a</sup> Determined using ICP-OES, <sup>b</sup> BET, <sup>c</sup> XRD using Scherrer equation.



Fig. 1. PXRD patterns of a) calcined 2 wt% Ru CeO2 catalysts and b) CeO2 supports.



Fig. 2. TEM images of reduced 2 wt% Ru supported a) CeO<sub>2</sub>-SA, b) CeO<sub>2</sub>-NR, c) CeO<sub>2</sub>-NC catalysts, and d) EDX-mapping of 2Ru/CeO<sub>2</sub>-NC.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

#### 3.1.1. Structural and textural properties

Fig. 1 shows the XRD patterns of the CeO<sub>2</sub> supports and synthesized 2 wt% Ru/CeO2-(SA/NR/NC) catalysts. The measured structure and physiochemical properties for the synthesized catalysts is given in Table 1. XRD patterns and physiochemical properties of the various metal loadings is given in Fig. S1 and Table S1. As observed from the XRD patterns, all of the samples exhibit characteristic peaks of the facecentered-cubic fluorite CeO2 structure (JCPDS 43-1002). Regardless of the metal loading, reflections corresponding to RuO2 or any other Ru containing phase were not observed in the CeO<sub>2</sub> catalysts, indicating that RuO<sub>x</sub> species are present as highly dispersed nanoparticles. Broader reflections in CeO2-NR are ascribed to their nanocrystalline nature, and the narrow intense reflections for the cube-shaped CeO<sub>2</sub> imply their larger sizes, corresponding with previous literature [73]. The averaged crystallite size of the prepared materials, calculated using the Scherrer equation, were found to be 8 nm for CeO2-NR, 20 nm for CeO2-NC, and 21 nm for CeO<sub>2</sub>-SA. Additionally, for all catalysts, the Ru loading, measured by ICP-OES, was found to be close to the nominal values within error. The BET specific surface areas were inversely proportional to crystallite size with 98, 41, and 35  $m^2g^{-1}$  for CeO<sub>2</sub>-NR, CeO<sub>2</sub>-SA, and CeO2-NC respectively. The corresponding N2 adsorption/desorption isotherms, given in Fig. S2-S4, show Type IV isotherms, which indicate the presence of mesopores [74]. A slight decrease in surface area was noted with the series of 0.5–5 wt% Ru/CeO<sub>2</sub> catalysts, regardless of morphology, which indicates a partial filling of pores by dispersed  $RuO_x$  species.

TEM was used to confirm the morphology of the prepared CeO<sub>2</sub> and image the dispersed Ru species. Fig. 2 presents the TEM micrographs of 2Ru/CeO<sub>2</sub>-(SA/NR/NC) catalysts at different magnification scales. The micrographs of 2Ru/CeO<sub>2</sub>-SA (Fig. 2a) display a mixture of spherical, rod, cube, rhombus, and trapezoid shapes of CeO<sub>2</sub> with measured Ru nanoparticles were 1–3 nm in range. Fig. 2b corresponds to the 2Ru/ CeO<sub>2</sub>-NR catalyst and confirms the well-defined porous nanorod morphology, with diameters between 5 and 10 nm and a length of 50–160 nm, resulting in aspect ratios greater than 20. No Ru particles are noted at 2 wt% loading, indicating Ru is present either as subnanometer clusters or adatom species. Images of 2Ru/CeO<sub>2</sub>-NC in Fig. 2c confirm the nanocube morphology, with sizes ranging between 20 and 70 nm. STEM-EDX color mapping of the 2Ru/CeO<sub>2</sub>-NC, shown in Fig. 2d, further confirm the presence of highly dispersed Ru.

Given the difficulties in observing Ru particles or clusters at lower loadings ( $\leq 2$  wt%), particularly in case of 2Ru/CeO<sub>2</sub>-NR, STEM-HAADF analysis on reduced catalysts with higher Ru loading (5Ru/CeO<sub>2</sub>-(NR/ NC)) was undertaken. As observed from Fig. 3a, Ru nanoclusters < 1 nm in size on the surface and edges of CeO<sub>2</sub>-NR are noted. The reduced 5Ru/ CeO<sub>2</sub>-NC, shown in Fig. 3b, exhibits Ru nanoclusters < 1.5 nm in size. However, the imaging and determination of smaller Ru clusters and adatoms remained difficult using microscopy techniques due to the poor contrast between Ru and CeO<sub>2</sub>, and representative particle size distributions were difficult to ascertain. Therefore, the combination of both



Fig. 3. HAADF-STEM images of reduced a) 5Ru/CeO2-NR and b) 5Ru/CeO2-NC catalysts. Arrows indicate positions of sub-nanometer Ru particles.



Fig. 4. H<sub>2</sub>-TPR profiles of a) different CeO<sub>2</sub> supports and b) 2 wt% Ru-supported CeO<sub>2</sub> catalysts.

 Table 2

 Reduction behaviour of different xRu/CeO<sub>2</sub>-(SA/NR/NC) catalysts.

Catalyst	RuO <sub>x</sub> Red <sup>n</sup> Tmax. (°C) <sup>a</sup>	$RuO_x H_2$ consumption (µmol/g) <sup>b</sup>		$RuO_x$ theoretical $H_2$ consumption $(\mu mol/g)^c$	${ m RuO_x}$ Total ${ m H_2}$ consumption ${(\mu mol/g)}^d$	CeO <sub>2</sub> surface H <sub>2</sub> consumption (µmol/g) <sup>e</sup>	CeO <sub>2</sub> bulk H <sub>2</sub> consumption (μmol/g) <sup>f</sup>	
		(30–110 °C)	(110–230 °C)		-	(240–500 °C)	(500–800 °C)	
CeO <sub>2</sub> -SA	-	-	-	-	-	106	445	
CeO2-NR	-			-	-	242	359	
CeO2-NC	-			-	-	143	581	
2Ru/CeO <sub>2</sub> - SA	131	111	333	384	444	66	653	
2Ru/CeO <sub>2</sub> - NR	85	568	185	277	753	141	667	
2Ru/CeO <sub>2</sub> - NC	80	311	192	344	503	77	584	

<sup>a,d</sup> From H<sub>2</sub>-TPR profile, <sup>b</sup> From H<sub>2</sub>-TPR peak integration from temperature 30–230 °C, <sup>c</sup> From the equation  $RuO_2 + 2 H_2 \rightarrow Ru + 2 H_2O$ , <sup>e</sup> H<sub>2</sub>-TPR peak integration from temperature 240–500 °C, <sup>f</sup> From H<sub>2</sub>-TPR peak integration from temperature 500–800 °C.

the TEM and CO chemisorption (*vide infra*) was needed to determine the enhancement of Ru dispersion on the shaped catalysts when compared to the unshaped catalyst.

the respective surface species is 1.3–2.2 fold higher on the shaped particles than on CeO<sub>2</sub>-SA.

#### 3.1.2. Catalyst reducibility

H<sub>2</sub>-TPR was initially used to determine the effects of CeO<sub>2</sub> morphology on the reducibility of surface oxygen and bulk oxygen and this is shown in Fig. 4a. The H<sub>2</sub> consumption on different CeO<sub>2</sub> morphologies as a function of temperature is given in Table 2. The reduction profile of the CeO<sub>2</sub> supports exhibits two peaks with the lower temperature peak assigned to surface reduction and the higher temperature peak attributed to bulk CeO2 reduction [75]. CeO2-SA displays two peaks with an intense surface reduction peak at 406 °C, and a broad bulk reduction peak at 676 °C. The shaped CeO<sub>2</sub> with defined facets showed similar H2-TPR profiles with surface reduction peaks at 400 and 361 °C, and bulk reduction at 678 and 682 °C for CeO2-NR and CeO2-NC respectively. It should be noted that the surface of CeO<sub>2</sub>-NC is reduced at a much lower temperature (361 °C) compared to CeO<sub>2</sub>-SA (406 °C) and CeO<sub>2</sub>-NR (400 °C) and is associated with the high oxygen mobility and lower oxygen vacancy formation energy of the expressed {100} surface facet [51,73,76]. In addition, the absolute amount of  $H_2$  consumed by

H<sub>2</sub>-TPR was then used to determine the effect of support morphology on the speciation and consequent reduction of the dispersed RuO<sub>x</sub> species, with 2Ru/CeO<sub>2</sub> given in Fig. 4b and data in Table 2. Other metal loadings are shown in Fig. S5 and Table S2. It is well known that RuO<sub>x</sub> species are reduced below 200 °C and their reduction temperatures vary depending on the metal-support interaction and Ru loading [77]. For comparison, the reduction profile of bulk RuO<sub>2</sub> (99.9% metal basis) displays a very broad peak centered around 150 °C (Fig. S6) with total  $H_2$  consumption of 17850 µmol g<sup>-1</sup> (theoretical 19603 µmol g<sup>-1</sup>) and 91% total reduction. In the  $H_2$ -TPR of the catalysts, dispersed  $RuO_x$ reduction occurs in the temperature range of 30-230 °C. The presence of multiple reduction peaks for RuOx confirms the presence of multiple RuO<sub>x</sub> species of varied interaction with CeO<sub>2</sub> with various cluster sizes [50]. The peaks in the low temperature region (30–110 °C) are ascribed to the reduction of different types of highly-dispersed cationic species of Ru having weak interaction strength with CeO<sub>2</sub>, while those in the temperature range (110-230 °C) are assigned to moderate to strong interaction of Ru with surface and/or sub-surface CeO<sub>2</sub> [78].

Note that for the xRu/CeO<sub>2</sub>-SA catalysts, the intensity of the first

peak at temperature below 100 °C remains small irrespective of Ru loading, while the second peak present around 130 °C increases with increasing Ru loading (Fig. S5a). Whereas, xRu/CeO<sub>2</sub>-(NR/NC) catalysts display very different reduction profiles (Fig. S5b-c). Interestingly, at 2 wt% Ru loading (Fig. 4b), the reduction peak, appearing around 109 °C in 2Ru/CeO2-SA catalysts, shifts to lower temperatures (80-85 °C), with an increase in intensity in the 2Ru/CeO2-NR and 2Ru/ CeO<sub>2</sub>-NC. This infers the presence of significant proportion of surface Ru species in weak interaction with CeO2. This is also evidenced by the higher H<sub>2</sub> consumption values of 111 vs 568, 311  $\mu$ mol g<sup>-1</sup> for 2Ru/ CeO<sub>2</sub>-SA, 2Ru/CeO<sub>2</sub>-NR and 2Ru/CeO<sub>2</sub>-NC respectively. The total H<sub>2</sub> consumption for RuO<sub>x</sub> in xRu/CeO<sub>2</sub>-NR catalysts was much greater than CeO2-SA-based catalysts by a factor of three at low loadings and 1.5 times at high loadings. This shows the shaped catalysts facilitate a smaller Ru particle size with smaller particles exhibiting a greater M-H bond strength, resulting in higher surface H\* coverage [22,79].

The total H<sub>2</sub> consumption values for RuO<sub>x</sub> species for all catalysts increase with metal loading and greatly exceed the theoretical consumption values by a factor of 2, showing H-spillover onto the CeO<sub>2</sub> support. This is also evidenced by the lower reduction temperature (265–288 °C) of the CeO<sub>2</sub> surface when impregnated with Ru. Such significant H-spillover phenomenon reflects the generation of oxygen vacancies and the formation of surface hydroxyl groups [80]. Additionally, it is a direct consequence of the electronic metal support interaction between CeO<sub>2</sub> and the dispersed Ru species [81]. H-spillover has been shown to be favorable for the hydrogenation of alkane species resulting in high activity for polyolefin hydrogenolysis [82]. It was found that metal loading exerts a negligible effect on the bulk CeO<sub>2</sub> reduction in all the CeO2-(SA/NR/NC), implying that most of the Ru species are located on the surface or sub-surface of the CeO2. To summarize, the shaped CeO2 supports not only affect the reducibility of RuOx species but also led to the generation of different types of Ru species bearing weak to strong interaction strength with the support and have increased H-spillover compared to the non-shaped CeO<sub>2</sub>.

#### 3.1.3. Ru dispersion

CO pulse chemisorption measurements were undertaken to estimate the Ru metal dispersion, the average Ru particle size, and the Ru surface area per gram of metal on different catalysts. The collated data for 2Ru/CeO<sub>2</sub> is shown in Table 3, with the supports and various metal loadings given in Table S1. The catalysts were reduced in 5%  $H_2/N_2$  at 300 °C for 30 min to reduce RuO<sub>x</sub> species to Ru(0) (evidenced by TPR *vide supra*). CO pulse experiments were also performed on pristine CeO<sub>2</sub>-(SA/NR/NC) supports and this results in a negligible amount of CO consumed, indicating that CO does not adsorb on the pristine supports under the reduction conditions used.

As observed from the CO chemisorption results, the shaped CeO<sub>2</sub>-supported catalysts with well-defined surface facets (xRu/CeO<sub>2</sub>-NR and xRu/CeO<sub>2</sub>-NC) exhibited remarkably high dispersion compared to the standard catalysts (xRu/CeO<sub>2</sub>-SA). Metal dispersion in 2Ru/CeO<sub>2</sub>-SA, 2Ru/CeO<sub>2</sub>-NR and 2Ru/CeO<sub>2</sub>-NC was 23%, 100%, and 72% respectively, with calculated Ru particle sizes of 5.7, 1.3, and 1.8 nm. The dispersion is calculated assuming the linear interaction of one Ru atom binding to one CO molecule with stoichiometry factor of 1. It is

#### Table 3

Ru dispersion, metal surface area, and Ru particle size measured by CO chemisorption.

-						
Catalyst	Dispersion (%D)	Metal surface area, $A_m$ ( $m^2 g_{metal}^{-1}$ )	Ru particle size (nm), S <sub>m</sub> (nm)			
2Ru/CeO2-SA	23	87	5.7			
2Ru/CeO2-NR	100	365	1.3			
2Ru/CeO2-NC	72	264	1.8			

From CO-Pulse experiments after reduction at 300  $^\circ\text{C}$  (See Table S3 for equations).



Fig. 5. CO-Pulse experiments Ru dispersion vs reduction temperature of 2Ru/CeO<sub>2</sub>-(SA/NR/NC) catalysts.

important to note that the formation of multiple Ru(CO)<sub>3</sub> species and CO dissociation is common and therefore the dispersions calculated using a stoichiometry factor of 1 can lead to error in dispersion values [83,84]. Additionally, CO can spillover onto oxygen vacancies and react with CeO<sub>2</sub> surface oxygen at the metal-CeO<sub>2</sub> interface forming adsorbed carbonate species [85-87]. However, despite these considerations, at any Ru loading studied, the CO uptake and calculated dispersions are significantly higher for the shaped Ru/CeO<sub>2</sub> catalysts than the non-shaped. The CO uptake was also observed to increase with increasing Ru loading, except for Ru/CeO2-NC where a drop from 143 to 117  $\mu$ molg<sup>-1</sup> is observed beyond 2 wt% Ru. For xRu/CeO<sub>2</sub>-NR and xRu/CeO<sub>2</sub>-NC, decreasing the Ru loading from 2 to 0.5 wt% leads to calculated dispersion values exceeding 100%. This also indicates multiple binding of CO to one Ru atom is occurring at lower loading, inferring the presence of sub-nanometer Ru species with an average Ru particle size smaller than 1 nm [88].

To further confirm the higher dispersions obtained on the shaped catalysts and to quantify the different Ru species as observed in the H2-TPR, a study of the effect of reduction temperature on the dispersion of Ru species for 2 wt% Ru/CeO2-(SA/NR/NC) was undertaken (Fig. 5; Table S3). For comparison, CO chemisorption of the non-reduced samples were also examined, resulting in a small CO uptake with Ru dispersion of 7.9%, 41.5%, and 32.8% for 2Ru/CeO2-SA, 2Ru/CeO2-NR and 2Ru/CeO2-NC respectively. Reduction at 100 °C gives an increased Ru dispersion with values of 20.3%, 65.2%, and 77.8% for 2Ru/CeO2-SA, 2Ru/CeO<sub>2</sub>-NR and 2Ru/CeO<sub>2</sub>-NC respectively, which corresponds to the peaks in the temperature range (30–110 °C) of the H<sub>2</sub>-TPR profiles (Fig. 4). This confirms a large proportion of Ru is accessible at low reduction temperatures in the shaped catalysts. With an increase in reduction temperature to 200 °C, Ru dispersion was almost doubled in 2Ru/CeO2-NR (~100%), with little difference in the 2Ru/CeO2-SA (20.3-28.8%) and 2Ru/CeO2-NC (77.8-72.8%). Reduction at 200 °C, below the reduction temperature of surface CeO<sub>2</sub>, should result in reduced CO spillover, indicating the high dispersions can be attributed to Ru species. No significant change in dispersion was observed by increasing the reduction temperature to 300 °C for all three catalysts confirming complete reduction of RuO<sub>2</sub> to Ru above 200 °C.

To summarize, Ru species were successfully dispersed on  $CeO_2$  supports regardless of morphology. However, the shaped particles (NC and NR) expressing defined surface facets, significantly enhanced Ru dispersion, particularly on CeO<sub>2</sub>-NR, with higher CO uptake values than the non-shaped Ru/CeO<sub>2</sub>. The higher dispersion was confirmed over a range of reduction temperatures and this confirmed a higher fraction of reduced Ru species is available on the shaped oxides. In addition, the shape and type of surface facet was crucial for the enhanced dispersion



Fig. 6. XPS spectra of a) C 1 s, Ru 3d, Ce 4 s and b) Ce 3d core levels of reduced and passivated 2Ru/CeO<sub>2</sub> catalysts.

of the metal species, when compared to the surface area and crystallite size. This is evidenced with the differences in dispersion of the *x*Ru/CeO<sub>2</sub>-SA and *x*Ru/CeO<sub>2</sub>-NC despite similar surface areas (29–44 and 25–35 m<sup>2</sup>g<sup>-1</sup>) and crystallite size (19–21 and 20–24 nm). Although, a slight enhancement in the Ru dispersion for *x*Ru/CeO<sub>2</sub>-NR over *x*Ru/CeO<sub>2</sub>-NC can be attributed to the secondary effects of support surface area and crystallite size.

#### 3.1.4. Catalyst speciation

In order to determine the speciation of the catalysts, XPS analysis of the fresh and reduced 2Ru/CeO2 catalysts was undertaken. The spectra for the Ru 3d and Ce 3d regions of the reduced catalysts given in Fig. 6 and the fresh catalysts are given in Fig. S7. The full component binding energies and atom percentages are given in Table S4. It should be noted that the Ru 3d region overlaps in energy with the C 1 s and the Ce 4 s regions and therefore complicate the deconvolution of the spectra [89]. A high carbon coverage is noted due to the sample exposure to air and potential surface carbonates arising from the hydrothermal synthesis method used to produce the shaped CeO2. The low Ru 3d signal is a function of the low metal loading (1.40-1.94 wt% by ICP-OES), although, deconvolution could be conducted due to the binding energy of the Ru 3d<sub>5/2</sub> peak being lower in energy than the C-C/C-H peak. Analysis of the Ru 3d doublet components was conducted using asymmetric line shapes, splitting of the spin-orbit components (4.17 eV), and constraints of the FWHM of the components to account for Coster-Kronig broadening of the 3d<sub>3/2</sub> peak, in correspondence with model compounds [90]. In all of the fresh catalysts (Fig. S7), the Ru  $3d_{5/2}$  component shows a binding energy of 280.6–281.3 eV corresponding to Ru(IV)O2. It is also important to note that any higher oxidation state Ru or  $Ru^{\delta+}$  species were not fitted due to the large carbon component, overlapping species, and the potential for RuO<sub>2</sub> satellite peaks. Interestingly, the shaped catalysts exhibit Ru 3d components with a shift to higher binding energy (281-281.3 eV) and a higher at% (1.07-1.85 at%) compared to the non-shaped catalyst (280.6 eV; 0.80 at%). This indicates a smaller particle size and increased electronic interaction with the support [49], in correlation with the TPR and CO chemisorption results. After reduction at 300 °C for 2 h followed by passivation in 1% air/Ar for 60 mins, the formation of a new Ru species at 279.8-280.6 eV is noted and is assigned to the formation of Ru(0) (Fig. 6a). The shift in binding energy and higher at% remained consistent in the Ru species of the reduced shaped catalysts compared to the non-shaped. The presence of a lower

percentage (30–46% of total Ru components) of surface RuO<sub>2</sub> can be rationalized to be a consequence of the passivation procedure (1% air/Ar). Reduction of this passivating surface RuO<sub>2</sub> layer is expected under the hydrogenolysis reaction conditions (220–280 °C, 10–30 bar H<sub>2</sub>), as noted in the TPR study. Therefore, Ru(0) is considered as the active catalytic species present during the catalytic reactions.

The electronic structure of Ce gives rise to various initial and final state effects leading to a complex Ce 3d spectrum. Thus, the deconvolution of the spectra was undertaken using a complex peak model initially comprising of literature values to constrain fitting parameters and account for the various states [91,92]. Following an initial fit, a slight relaxation of the FWHM and binding energy constraints of the peak model was allowed. This was to allow the model to account for distortions in local structure arising from heterogeneous surface defects and differences in particle size between samples, both of which can lead to alterations in charge transfer processes, and differences in instruments between studies. Specifically, for the reduced Ru/CeO2-SA (Figs. 6b), four symmetric peaks at 880.6, 885.2, 898.7, and 903.9 eV are attributed to the  $v^0$ ,  $v^I$ ,  $u^0$ ,  $u^I$  states of Ce(III), whereas six asymmetric-like peaks at binding energies 882.3, 888.5, 898.1, 900.7, 907.3, and 916.3 eV are assigned to the v,  $v^{\rm II},v^{\rm III}$  and u,  $u^{\rm II},u^{\rm III}$  states of Ce(IV). The assignment of components in the Ce 3d region remains the same for all the fresh catalysts (Fig. S7) and reduced Ru/CeO<sub>2</sub>-NR and Ru/CeO2-NC catalysts (Fig. 6b). The presence of surface Ce(III) in both fresh and reduced bulk CeO2 is not unexpected due to the formation of oxygen vacancies, surface hydroxyls, and hence surface defects [44]. Given the XRD patterns of the catalysts correspond to the bulk CeO2 phase with confirmation of the morphology by TEM, the presence of a small percentage of Ce(III) is attributed to Ce<sub>2</sub>O<sub>3</sub> or Ce(OH)<sub>3</sub> surface defects rather than a mixture of phase separated materials. For the reduced and passivated catalysts, Ce(III) defects ranged between 6% and 8% of total Ce components, although, it is also anticipated that further CeO2 surface reduction will occur during hydrogenolysis reactions through H-spillover.

The characterization methods presented therefore show that the shaped particles enhance Ru dispersion as shown by CO chemisorption, with the catalytic species present in the catalytic reactions determined to be Ru(0) by XPS. Additionally, H<sub>2</sub>-TPR and XPS showed the shaped particles alter the metal-support interaction between Ru and CeO<sub>2</sub> which leads to increased H-spillover when compared to the non-shaped. The XRD patterns of the catalysts were assigned the bulk structure of the

support to CeO<sub>2</sub>, although, XPS analysis confirmed the presence of surface Ce(III) defects in the Ru/CeO<sub>2</sub> catalysts which arise from undercoordinated Ce sites formed by surface hydroxylation or oxygen vacancies from the support synthesis, particle size, interaction with Ru species, or reduction by  $H_2$ .

#### 3.2. Catalytic hydrogenolysis results

## 3.2.1. Hydrogenolysis of pristine low-molecular weight polypropylene (i-PP-12 K)

The series of synthesized catalysts (xRu/CeO<sub>2</sub>-(SA/NR/NC)) were applied to the hydrogenolysis of low molecular weight isotactic polypropylene (i-PP-12 K, Mw: ~12000 Da and Mn: ~5000 Da). The reaction products in this study are designated as solid, liquid or gas products. Solid products consist of unreacted polymer and CH<sub>2</sub>Cl<sub>2</sub> insoluble solid polymer products. Therefore, solid conversion is a measure of the formation of liquid and gas products rather than initial polymer conversion. Liquid products allude to CH<sub>2</sub>Cl<sub>2</sub> soluble products that are liquids or oligomer waxes at room temperature. Additionally, due to the inherent branching of PP, complex mixtures of liquid products are obtained, resulting in difficulties in quantitative GC-MS analysis, as shown in the qualitative GC-MS analysis of a PP-12 K reaction at 250  $^\circ\text{C}$  in Fig. S8. However, the GC-MS analysis confirms the presence of C<sub>6</sub>-C<sub>27</sub> hydrocarbons as well as oligomer waxes. Subsequently, analysis of the liquid products was undertaken using GPC to give average M<sub>w</sub>, M<sub>n</sub>, and polydispersity indexes. Gas products refers to C1-C5 alkanes analysed from the reactor headspace. Investigation of the reaction parameters (temperature, metal loading, and H2 pressure) were conducted at fixed reaction times to investigate the importance of these parameters on different product yields and to control the average M<sub>w</sub> of the liquids

obtained over highly active catalysts. The obtained optimized parameters were then used in a time course study to evaluate product evolution and liquid chain length as a function of time.

3.2.1.1. Effect of metal loading. The effect of metal loading on the overall product distribution and percentage depolymerization in PP hydrogenolysis was investigated using different Ru loadings (0.5, 1, 2, and 5 wt%) on CeO<sub>2</sub>-(SA/NR/NC) catalysts. Increasing the metal loading on the catalysts results in both geometric effects through particle size growth, as evidenced by a reduction in Ru dispersion, and alteration of the active metal-substrate ratio with more sites available for reaction. Fig. 7 plots the yields of different products and the average M<sub>w</sub> distribution, while Table S5 and Fig. S9 summarize the catalytic results and gas product distribution respectively. In general, increasing the metal content enhanced polymer depolymerization (up to 90-94% at 5 wt% Ru) for all catalysts. However, high Ru content facilitates the depolymerization into gaseous products, with higher gas yields (34-49%) over 5 wt% catalysts (Fig. 7a-c). This can be rationalized to be due to both increased particle size favoring terminal chain cleavage to form methane (computational study vide infra) and a greater number of sites available for reaction. An increased concentration of active sites increases the amount of secondary hydrogenolysis reactions, which results in shorter liquid chains [93]. This is shown in the decrease in  $M_w$  of the liquid products as function of loading and the eventual formation of gaseous products (Fig. 7d).

For all catalysts, 1 wt% Ru loading was found to achieve the highest liquid yield and reaction rates, with the highest liquid yields achieved over the shaped catalysts. However, it is important to note that due to the complexity of PP hydrogenolysis, it is insufficient to describe catalytic activity purely through liquid yields or liquid productivity, due to



Fig. 7. Effect of Ru loading on product distribution in PP hydrogenolysis for xRu supported a) CeO<sub>2</sub>-SA b) CeO<sub>2</sub>-NR, c) CeO<sub>2</sub>-NC catalysts, and the d) M<sub>w</sub> distribution of the liquid fraction of products for each catalyst. Reaction conditions: i-PP-12 K - 2 g, Catalyst - 0.1 g, Temperature - 220 °C, Time - 16 h, H<sub>2</sub> - 30 bar (R.T.), RPM - 500.



Fig. 8. Effect of reaction temperature on product distribution in PP hydrogenolysis for 2 wt% Ru supported a) CeO<sub>2</sub>-SA b) CeO<sub>2</sub>-NR, c) CeO<sub>2</sub>-NC catalysts, and the d) M<sub>w</sub> distribution of the liquid fraction of products for each catalyst. Reaction conditions: i-PP-12 K - 2 g, Catalyst - 0.1 g, Temperature - 180–250 °C, Time - 16 h, H<sub>2</sub> - 30 bar (R.T.), RPM - 500.

the varying composition of the liquid phase from secondary reactions. The chain lengths and distribution of the resultant liquid product must also be considered when evaluating catalyst performance. Therefore, when considering the production of lighter hydrocarbons with a smaller PDI, at a slight expense of liquid yield (68–70% over shaped catalysts), a Ru loading of 2 wt% was considered as optimal for all the catalysts. The shaped catalysts, in particular the NC catalysts, not only exhibit enhanced liquid yields but also show shorter liquid products (Fig. 7d) when compared to the non-shaped catalyst over metal loadings up to 2 wt%, confirming the higher activity of the shaped catalysts.

3.2.1.2. Effect of temperature. Fig. 8 shows the product yield and liquid average M<sub>w</sub>, obtained in the hydrogenolysis of i-PP-12 K as a function of temperature (180-250 °C) for the three 2Ru/CeO<sub>2</sub> catalysts; Table S6 lists the catalytic results and Fig. S9 shows gas distribution. At 180 °C, the 2Ru/CeO<sub>2</sub>-SA catalyst (Fig. 8a) displayed no activity with recovery of the solid (99%). A similar product distribution was observed when the temperature was increased to 200 °C with 97% solid product recovery. In contrast, the 2Ru/CeO2-NR (Fig. 8b) and 2Ru/CeO2-NC (Fig. 8c) catalysts, under a reaction temperature of 200 °C, afforded up to 27% liquid yield with the formation of up to 9% gases and a reduced amount of solid product (67-68%). The shaped catalysts can thus deconstruct the pristine i-PP 12 K ( $M_w \sim 12,000$  Da) polymer to oligomers at 200 °C with M<sub>w</sub> values in the range 3158–6217 Da (Fig. 8d). The highest liquid yields of 68% and 70% were obtained at 220  $^\circ C$  with 62% and 87% depolymerization using 2Ru/CeO2-NR and 2Ru/CeO2-NC respectively. It was found that 2Ru/CeO2-NC not only has a greater ability to deconstruct the polymer, evident by the higher DP values, but also it is able to produce the liquid product comprising hydrocarbons of low M<sub>w</sub> values when compared to 2Ru/CeO2-NR and 2Ru/CeO2-SA catalysts

(Fig. 8d). Additionally, the 2Ru/CeO<sub>2</sub>-NC at 220 °C produced a more homogeneous molecular weight distribution (PDI = 1.56) than 2Ru/CeO<sub>2</sub>-NR (PDI = 2.37) and 2Ru/CeO<sub>2</sub>-SA (PDI = 2.42). With a further increase in temperature from 220 to 250 °C, the gas yields increase significantly from 10% to 27% to 57–72% at the expense of liquid product for all the three catalysts. The M<sub>w</sub> values of liquid products at 250 °C (Fig. 8d) exhibit the lowest value (< 434 Da) with less than 34% yield with GC-MS analysis (Fig. S8) of the liquid product confirming the formation of hydrocarbons ranging from C<sub>6</sub> to C<sub>27</sub>, encompassing linear and methyl-substituted alkanes for the 2Ru/CeO<sub>2</sub>-NR catalyst.

Considering the gas products formation as a function of reaction temperature (Fig. S10), the 2Ru/CeO<sub>2</sub>-SA catalyst exhibited the formation of gases (C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> & C<sub>4</sub>) at 250 °C. The production of the gas fraction can be assigned to the activity of the larger particles ( $\geq$  1.5 nm NP) preference for terminal C-C scissions. However, only methane and ethane are mainly formed for 2Ru/CeO<sub>2</sub>-NR and 2Ru/CeO<sub>2</sub>-NC catalysts resulting from secondary reactions of liquid products [93].

From the above results, it has been shown that the shaped catalysts have high activity at low temperatures (200–220 °C) when compared to the non-shaped catalyst, with yield towards liquid products maximized using this temperature range. Although, a reaction temperature of 220 °C was the best temperature to obtain liquid products at high yield, employing a lower reaction temperature of 200 °C and extending the reaction time could be helpful in optimising their yield and  $M_w$  distribution.

3.2.1.3. Effect of  $H_2$  pressure. The effect of  $H_2$  pressure (10, 20, and 30 bar at room temperature) was investigated with 2Ru/CeO<sub>2</sub>-(SA/NR/NC) in the i-PP-12 K hydrogenolysis at 220 °C and 16 h and is shown in Fig. 9a-c. Table S7 compiles the results and Fig. S9 represents the gas



Fig. 9. Effect of  $H_2$  pressure on product distribution in PP hydrogenolysis for 2 wt% Ru supported a) CeO<sub>2</sub>-SA b) CeO<sub>2</sub>-NR, c) CeO<sub>2</sub>-NC catalysts, and the d)  $M_w$  distribution of the liquid fraction of products for each catalyst. Reaction conditions: i-PP-12 K - 2 g, Catalyst - 0.1 g, Temperature - 220 °C, Time - 16 h,  $H_2$  - 10–30 bar (R.T.), RPM - 500.

distribution. For all catalysts, an increase in hydrogen pressure enhanced the reaction rate and liquid yield, correlating with Chen et al. [93]. For the 2Ru/CeO<sub>2</sub>-SA catalyst (Fig. 9a), no further increases were seen after 20 bar, with the highest liquid yield of 45%, indicating the higher hydrogen pressure could impede depolymerization [94]. However, this is not observed over the shaped catalysts (2Ru/CeO2-NR (Figs. 9b) and 2 Ru/CeO<sub>2</sub>-NC (Fig. 9c)) with a higher liquid yield at 10 bar (up to 44%) and a continual increase in the liquid yield (up to 70%) with increasing pressure. Additionally, the liquid yield obtained for the shaped catalysts at increased pressure consisted of a lower M<sub>w</sub> distribution (Fig. 9d), which is attributed to the conversion of the liquid alkanes in secondary reactions [93]. The lowest M<sub>w</sub> and M<sub>n</sub> values of 1531 and 984 Da were obtained at 30 bar with the 2Ru/CeO2-NC catalyst with 87% polymer depolymerization. The gas product distribution showed methane being formed as a major gas followed by ethane and propane at all pressures (Fig. S9), with an increase in gas yield (11-33%) only noted for 2Ru/CeO2-NC. The shaped catalysts were notably more active than 2Ru/CeO2-SA with similar liquid yields achieved (32-44%) at 10 bar rather than the liquid yields achieved at 20-30 bar (43-45%) for the 2Ru/CeO2-SA. This shows the high dispersion of the Ru species with disordered clusters is important in both catalytic activity and surface \*H coverage, in agreement with Chen et al. [95], with the shaped catalysts significantly more active at all pressures tested. It was also shown that 30 bar initial hydrogen pressure results in the highest reaction rates and liquid yield for the catalysts and is therefore used throughout the study.

3.2.1.4. Effect of reaction time. The effect of reaction time was studied on hydrogenolysis experiments performed between 8 and 24 h at 220  $^{\circ}$ C and 16–60 h at 200  $^{\circ}$ C. Fig. 10 and Fig. S11 represents the total product distribution and the gases formed in the hydrogenolysis of i-PP 12 K for

the catalysts at the two different reaction temperatures and Tables S8-S9 list the catalytic results. The liquid and gas yield for the 2Ru/CeO2-SA catalyst at 220 °C increased linearly with reaction time from 8 to 24 h with concomitant decrease in the liquid Mw values from 12,000 to 4000 Da (Fig. 10a). It is important to note, that the decrease in  $M_{\rm w}$ values of the polymer and resultant liquids lead to variability in reaction viscosity and hence any mass transport influence is altered as the reaction progresses. Similar trends were observed in 2Ru/CeO2-NR (Fig. 10b) with a linear increase in liquid yield from 40% to 70% for 8 and 16 h and then remained constant thereafter. Although, despite a maximum in liquid yield, the liquid chain length shortens as the reaction progresses due to secondary hydrogenolysis reactions. In contrast, 2Ru/ CeO<sub>2</sub>-NC catalysts (Fig. 10c) resulted in a high liquid yield (60%) and the smallest  $M_W$  (3540 Da) at a reaction time of 8 h, with the highest reaction rate of 101.3  $g_{PP}h^{-1}g_{metal}^{-1}$ . The gas distribution showed that methane was the major gas, in line with the modelling findings, and the proportion of the gases increased with longer reaction time (Fig. S11ac). Furthermore, the 2Ru/CeO2-NC catalysts afforded a liquid product with the lowest M<sub>w</sub> and M<sub>n</sub> values (652 and 548 Da) after 24 h, with PDI values near to one, indicating homogeneity in the liquid product. The higher activity of the shaped catalysts can be attributed to the increased dispersion and production of disordered Ru species, in-agreement with Chen et al. [95], and the electronic effects of the metal-support interaction as evidenced by the TPR results and corresponding with Lu et al. [55]. The catalytic results presented show the reaction time can be used to control of the liquid chain length whilst maintaining the high liquid yields achieved by the highly active catalysts.

A time study at a lower reaction temperature of 200  $^{\circ}$ C was also conducted to measure the effect on yields and chain length at reduced reaction rates. In this case, the 2Ru/CeO<sub>2</sub>-NR catalyst (Fig. 10e) remained the most selective among the three catalysts, giving the



Fig. 10. Effect of reaction time on product distribution in PP hydrogenolysis at 220 °C for 2 wt% Ru supported a) CeO<sub>2</sub>-SA b) CeO<sub>2</sub>-NR, c) CeO<sub>2</sub>-NC catalysts and at 200 °C for 2 wt% Ru supported d) CeO<sub>2</sub>-SA e) CeO<sub>2</sub>-NR, f) CeO<sub>2</sub>-NC catalysts. M<sub>w</sub> distribution of the liquid fraction of products for each catalyst is given at each liquid yield data point. Reaction conditions: i-PP-12 K - 2 g, Catalyst - 0.1 g, Temperature - 200–220 °C, H<sub>2</sub> - 30 bar (R.T.), RPM – 500.



Fig. 11. Reusability study of 2Ru/CeO<sub>2</sub>-(SA/NR/NC) in the hydrogenolysis of i-PP-12 K, with product distribution for fresh and reused catalyst. Reaction conditions: i-PP-12 K - 2 g, Catalyst- 0.1 g, Temperature - 220 °C, Time - 16 h, H<sub>2</sub> - 30 bar (R.T.), RPM - 500.

highest liquid yield at 60 h of 75% with  $M_w$  values of 1509 Da. In contrast, the 2Ru/CeO<sub>2</sub>-SA catalyst (Fig. 10d) only showed activity from 24 h with 20% liquid yield, which increased to 62% at 60 h with  $M_w$  of 3182 Da. The liquid obtained over the 2Ru/CeO<sub>2</sub>-NC (Fig. 10f) at 60 h (68%), comprised of hydrocarbons with the lowest  $M_w$  of 557 Da. Interestingly, the gas formation was suppressed at 200 °C (20%) compared to 220 °C (44%) over the 2Ru/CeO<sub>2</sub>-NC at similar solid conversions (88% vs. 92%). Therefore, alteration of the reaction temperature and time not only affects the catalytic rates but can be utilized to tune the  $M_w$  of the liquid product whilst maintaining or even increasing the liquid yields, especially over the highly reactive 2Ru/CeO<sub>2</sub>-NC catalyst.

3.2.1.5. Recyclability study. The reusability of the catalysts was studied by recovering the spent catalysts, followed by a regeneration procedure, and a subsequent second hydrogenolysis reaction of i-PP-12 K. The regeneration procedure consisted of washing the spent catalysts with DCM and drying at ambient temperature, followed by calcination at 500 °C, for 4 h, and finally reduction under 10% H<sub>2</sub>/Ar at 300 °C for 2 h. The calcination temperature (500 °C) ensures the complete removal of coke or unreacted polymer from the spent catalyst, however, this results in re-oxidization of the dispersed metallic Ru to RuO<sub>x</sub>, which necessitates the consequent reduction step. The reduction procedure for the reactivation is analogous to the reduction of the fresh catalysts and therefore it is anticipated to result in the formation of Ru(0), as evidenced by XPS of the fresh reduced catalysts. To confirm the stability of the Ru phases, the measured dispersions of the used catalysts (Table S10), indicate limited particle growth resulting from the regeneration procedure. Structural stability of the catalysts was confirmed using XRD (Fig. S12) with the patterns of the regenerated materials exhibiting no additional peaks when compared to the fresh catalysts. ICP (Table S10) results also reveal negligible leaching of Ru in all three catalysts. Fig. 11 and Table S11 represent the total product distribution for two reaction cycles with 2Ru/CeO<sub>2</sub>-(SA/NR/NC), with slight enhancement in depolymerization leading to lower  $M_w$  for both the SA and NR catalysts. Similar yields are obtained between catalytic cycles, showing the high catalytic stability of 2Ru/CeO<sub>2</sub>-(SA/NR/NC) over two cycles. Therefore, the characterization and catalytic results show the robustness of the catalysts in hydrogenolysis reactions.

#### 3.2.2. Mechanistic computational study

A computational DFT investigation was performed on the hydrogenolysis of a pentane (C<sub>5</sub>) molecule on the ruthenium surface to unravel the dominant presence of methane in the gas fraction observed in the experiment. On a pristine Ru(0001) surface, pentane adsorbs preferentially in a parallel position at an average height of  $\sim$ 3.40 Å from the surface, as shown in Fig. S15a. The most favorable H adsorption on the pristine surface is on an hcp hollow site with an average Ru–H distance of 1.89 Å (see Fig. S15b), in agreement with the literature [71]. The presence of hydrogen makes C<sub>5</sub> move slightly closer to the surface at  $\sim$ 3.35 Å.

The pentane hydrogenation process consists of approaching the molecule to the Ru(0001) surface in the presence of H-adatoms, followed by consecutive hydrogenations in different positions along the aliphatic chain: terminal (C1), second (C2), and central (C3) carbon in the molecule, leading to methane and ethane gas products. These lead to three different reaction pathways, as depicted in Fig. S16-S18 including key interatomic distances. Pentane adsorption and hydrogenation energies are represented in the thermodynamic profiles in Fig. 12, and the values are provided in Table S13.

The reaction pathway with the first hydrogenation on C1 is the most favorable and leads to methane products (Fig. S16). The C–C bond scission is a concerted process with the H transfer from the Ru surface to the molecule. The methane is formed and stays at 4.01 Å from the aliphatic chain, which strongly binds the Ru surface (distance Ru–C= 2.18 Å) to compensate for the dangling bond arising from –CH<sub>2</sub> ( $\Delta E$ = –0.09 eV). The consecutive hydrogenation of this new terminal carbon stabilizes the system ( $\Delta E$ = –0.78 eV), and it desorbs from the surface to enter a new hydrogenolytic cycle.

The second reaction pathway is the hydrogenation of C2 leading to



**Fig. 12.** Calculated thermodynamic profiles for the successive hydrogenations of  $C_5H_{12}$  on the Ru(0001) surface through the terminal (C1), second (C2), and central (C3) carbon in the molecule. The energy at 0 eV corresponds to the reference energy of Ru(0001) surface; and pentane and hydrogen isolated molecules.

ethane, as depicted in Fig. S17. Similar to the C1-pathway, the C2 hydrogenation drives the C-C bond scission leaving the aliphatic chain anchored to the Ru surface at a distance of 2.0 Å, while ethane hovers over the Ru surface at a distance of 4.38 Å. The reaction energy for this process is slightly more endothermic than the C1-pathway. Note that the process does not lead to methyl intermediates on the Ru surface. The hydrogenation of the original C3 site, now a new terminal carbon, releases the aliphatic chain from the Ru surface, which, together with ethane, lies at -0.70 eV with respect to the reference energy, i.e., Ru (0001) surface and isolated pentane and hydrogen molecules. The third reaction route is isoenergetic to the C2-pathway, with the exception of the second co-adsorbed H adatom (Fig. S18). The same energy profile implies that energy differences in adsorbing propyl or ethyl on Ru are balanced by the relative energies of ethane and propane hovering on the same surface. Our finding is in line with the recent investigation of hydrogenolysis of ethane and propane on Ru(0001) [96]. It can be noted that the hydrogenolysis process in their study is followed by multistep dehydrogenations and then C-C cracking, whereas in present study, we have studied successive hydrogenolysis at different carbons leading to the C-C bond scission.

Note that the reaction mechanisms for any catalytic process is not only dependent on the size and shape of the nanoparticles, but also intrinsically entangled to the availability of specific, low-coordinated sites, or the enhanced stability of reaction intermediates upon [97]. However, for an ideal Ru(0001) surface, both the surface atoms and the atoms underneath form hexagonal atomic layers. The low-energy electron diffraction (LEED) experiment gives a  $1 \times 1$  pattern for this system, indicating an unreconstructed surface [98]. Therefore, the Ru(0001) surface is an ideal termination of the bulk hcp crystal and all the surface sites for very large NPs can be represented by suitable periodic slab models as employed in the present study.

Despite the competitive pathways for the formation of methane and ethane, the computational results show preferential hydrogenolysis on terminal carbons of alkanes, hence, justifying the experimental observations of methane formation as the main product in the gaseous fraction upon polymer hydrogenolysis on Ru(0001) terraces, the most common face on medium and large NPs. In agreement with experiments, this result has implications on the time effects on the PP depolymerization, i.e., the longer the reaction, the higher the methane fraction in the gas phase. These results also shed some light on designing selective catalysts for alkane hydrogenolysis regarding the adsorption of unsaturated aliphatic chains.

### 3.2.3. Extension to large molecular weight PP and post-consumer PP plastics

Having encouraging results in the hydrogenolysis of low  $M_w$  i-PP-12 K ( $M_w$ : 12,000 Da) with 2Ru/CeO<sub>2</sub>-NR and 2Ru/CeO<sub>2</sub>-NC catalysts, the study was extended to large  $M_w$  polypropylene i-PP-250 K ( $M_w$ : 250,000 Da) and post-consumer polypropylene plastics. The hydrogenolysis of post-consumer PP plastics was conducted under the optimized reaction conditions (220 °C, 30 bar, 16 h) without the addition of pristine polymer to reduce reaction viscosity [30]. Table 4 compiles the results of the hydrogenolysis of pristine PPs (12 K and 250 K) and post-consumer plastics (PP-CT, PP-FS, and PP-FC). For comparison, results of 2Ru/CeO<sub>2</sub>-SA catalyst have also been added.

Analysis of the results show the shaped catalysts are highly active in deconstructing both high M<sub>w</sub> PP and the post-consumer plastics, with a high yield to liquid products (58–81%). The shaped catalysts exhibit lower gas and solid yields when compared to 2Ru/CeO<sub>2</sub>-SA. Interestingly, the high activity of 2Ru/CeO<sub>2</sub>-NC catalysts, which gave lower liquid yields when compared to 2Ru/CeO<sub>2</sub>-NR for low M<sub>w</sub> polymers, results in the highest liquid yields (77–81%) for larger M<sub>w</sub> plastics. Therefore, the M<sub>w</sub> and structure of the polymers must also be considered when using highly active catalysts for polymer hydrogenolysis. Overall, the liquid yield obtained for higher M<sub>w</sub> plastics was in the order of 2Ru/CeO<sub>2</sub>-NC catalyst

#### Table 4

Catalytic	performance	of 2Ru/C	eO <sub>2</sub> -(SA/N	IR/NC) i	n the	hydrogeno	lysis of	different	polypropy	lene p	lastics.
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0.1.1	Ru	PP Source	M <sub>w</sub> e (Da)	Mn		Solid Conversion (%)	Yield (%)			GPC of liquid product				Reaction rate by total metal			
Catalysis	(wt %)			(Da)	PDI		Gas	Liquid	Solid	M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	PDI	DP (%)	$(g_{PP \ depoly} \ h^{-1} \ g_{metal}^{-1})$			
		SA	12000	5000	2.4	53	10	43	47	5451	2256	2.41	54.6	35.2			
		SA	250000	67000	3.7	72	14	58	28	5050	1848	2.73	98.0	63.1			
CeO <sub>2</sub> -SA	1.94	CT	11975	5880	2.0	59	20	39	41	3214	1411	2.27	73.2	47.1			
				FS	20650	9365	2.2	70	16	54	30	5841	1975	2.95	71.7	46.2	
		FC	132280	36225	3.7	52	18	34	48	4369	1468	2.97	96.7	62.3			
	1.40	SA	12000	5000	2.4	80	10	70	20	4555	1924	2.35	62.1	55.4			
			SA	250000	67000	3.7	79	12	67	21	8648	2596	3.31	96.5	86.2		
CeO2-NR		CT	11975	5880	2.0	87	12	75	13	3346	1356	2.45	72.1	64.4			
		FS	20650	9365	2.2	75	10	64	25	5090	2368	2.14	75.3	67.3			
		FC	132280	36225	3.7	90	10	80	10	5525	2248	2.45	95.8	85.6			
					SA	12000	5000	2.4	95	27	68	5	1531	984	1.5	87.3	62.7
		SA	250000	67000	3.7	88	7	81	12	5584	2676	2.08	97.8	70.2			
CeO <sub>2</sub> -NC	1.74	CT	11975	5880	2.0	85	27	58	15	1519	728	2.09	87.3	62.7			
		FS	20650	9365	2.2	89	15	74	11	1662	1058	1.57	92.0	66.1			
		FC	132280	36225	3.7	90	12	77	10	2526	1342	1.88	98.1	70.5			

Reaction conditions: PP - 2 g, Catalyst- 0.1 g, Temp.- 220 °C, Time- 16 h, H<sub>2</sub>- 30 bar (R.T.), RPM - 500, Catalyst reduced at 300 °C for 2 h under 10% H<sub>2</sub>/Ar (50 mL min<sup>-1</sup>) ; SA- Sigma Aldrich, CT- Centrifuge Tube from laboratory, FS- File sheet from office, FC- Fragrance case from local market;  $M_{w}$ - weight average molecular weight from GPC; PDI - Polydispersity index =  $M_w/M_n$ .

also exhibited the lightest liquid hydrocarbons ( $M_w$ : 1519–5584 Da) with a low PDI (1.5–2.09).

To further assess the activity of the shaped catalysts, a comparison with existing literature for the hydrogenolysis of PP-250 K was undertaken and the comparative data is given in Table S14. This comparison shows the high activity of the shaped catalysts, in particular the Ru/CeO<sub>2</sub>-NC, at low loadings (nominally 2 wt%) under mild reaction conditions (220 °C), with an enhancement of liquid yield for dispersed Ru catalysts in the hydrogenolysis of high  $M_w$  PP.

#### 4. Conclusions

Shaped Ru/CeO<sub>2</sub> catalysts (nanorods or nanocubes) with low Ru loading have been investigated for the hydrogenolysis of polypropylene under mild reaction conditions and exhibit higher activity and liquid yield when compared to Ru/CeO<sub>2</sub> prepared using a non-shaped commercial support. The 2 wt% Ru/CeO<sub>2</sub> nanocube catalysts exhibited the highest ability to deconstruct polymer and oligomer chains to give high yields of liquid products with low M<sub>w</sub> and small polydispersity indices.

Alteration of the reaction conditions allowed for tuneability of both liquid yields and liquid chain length. Such control over chain lengths through the manipulation of reaction conditions could be exploited to widen the range of potential applications of the liquid products. The time course study demonstrated the ability of the shaped catalysts, with the nanocube catalyst showing the highest activity, to deconstruct the polymer, with the reaction time used to further control the chain lengths and maintain high liquid yields. Additionally, the lower reaction temperature of 200 °C resulted in suppression of gas yields (22% vs. 44%), with increased liquid yield and similar chain lengths over the highly active 2 wt% Ru/CeO2-NC at similar conversions (88% vs. 92%). Furthermore, the hydrogenolysis of large M<sub>W</sub> and post-consumer polypropylene under the optimized parameters resulted in a high liquid yield and large degree of depolymerization over the shaped catalysts. This shows the applicability of shaped catalysts to various substrates, with the potential for wider waste plastic substrate scope.

The enhanced activity and liquid yield achieved over shaped catalysts was attributed to the improved dispersion of Ru species when compared to the non-shaped Ru/CeO<sub>2</sub>, generating small highly active Ru nanoclusters. The generated sub-nanometer Ru species favored higher hydrogen adsorption which regulated the regioselectivity by breaking C-C internal bonds rendering a high liquid alkane yield. This was further confirmed using computational simulations to rationalize the large extent of methane formation in the gaseous fraction in the presence of medium and large Ru NPs on the non-shaped Ru/CeO<sub>2</sub> catalyst. The reduced Ru particle size effect is in-combination with higher H-spillover onto the shaped supports, leading to increased availability of hydrogen on the catalyst surface and improved the rate of C-C cleavage. Further investigation is underway to determine the importance and influence of surface facets exposed by the shaped CeO<sub>2</sub> materials in polyolefin hydrogenolysis.

#### CRediT authorship contribution statement

Ajay Tomer: Conceptualization, Methodology, Investigation, Writing – original draft. Mazharul M Islam: Methodology, Investigation, Writing – review & editing. Mounib Bahri: Investigation, Writing – review & editing. Donald R Inns: Methodology, Investigation, Writing – review & editing. Troy D Manning: Resources, Writing – review & editing. John B Claridge: Writing – review & editing. Nigel D Browning: Writing – review & editing. C Richard A Catlow: Funding acquisition, Conceptualization, Writing – review & editing. Alberto Roldan: Funding acquisition, Conceptualization, Supervision, Investigation, Writing – review & editing. Alexandros P Katsoulidis: Conceptualization, Supervision, Investigation, Writing – review & editing. Matthew J Rosseinsky: Funding acquisition, Conceptualization, Supervision, Investigation, Writing – review & edit-

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### **Data Availability**

The data collected for this work is available via the University of Liverpool data repository at 10.17638/datacat.liverpool.ac.uk/2182.

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#### Supporting information

The supporting information file contains tables with detailed catalysis results,  $N_2$  adsorption isotherms,  $H_2$ -TPR and schematics of the models used in the computational study.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcata.2023.119431.

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