

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental





A general strategy and a consolidated mechanism for low-methane hydrogenolysis of polyethylene over ruthenium

Cong Wang^a, Kewei Yu^b, Boris Sheludko^a, Tianjun Xie^a, Pavel A. Kots^a, Brandon C. Vance^{a,b}, Pawan Kumar^c, Eric A. Stach^c, Weiqing Zheng^a, Dionisios G. Vlachos^{a,b,*}

^a Center for Plastics Innovation, University of Delaware, 221 Academy St., Newark, DE 19716, USA

^b Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy St., Newark, DE 19716, USA

^c Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

ARTICLE INFO	A B S T R A C T
Keywords:	Polvethylene (PE) is one of the most environment-threatening plastic waste. Its Ru-catalyzed hydrogenolysis is
Plastic waste	rapid but produces too much methane. Here, low-density PE hydrogenolysis is performed at mild conditions and short times over Ru-doped zirconia catalysts (Ru-XZr, $X = Ti$, Nb, Ce, W, V, Mo, Fe) to determine low-methane catalysts. Methane is produced via direct terminal C-C scission and surface cascade of consecutive C-C scissions, with the latter sensitive to hydrogen availability and dominant in hydrogen-lean conditions. Reactivity studies,
Hydrogenolysis	
Ruthenium	
Doped oxide	
LOW INCUIANC	

characterization and theory reveal that the most effective dopant oxides (W, V, and Mo) are intermediately reducible, as they store and supply extra hydrogen to Ru via reverse hydrogen spillover. This hydrogen readily hydrogenates and desorbs long alkyl surface intermediates that would otherwise produce cascade methane. Our proposed mechanism reconciles the low methane production achieved by increasing the hydrogen pressure or reducing the particle size and exposes the key selectivity descriptors.

1. Introduction

Hydrogen spillover

The accumulation of primary plastic waste (PW) will double in about 15 years if the current use, discard, and recycle patterns persist. [1] Polyolefin (PO) plastics, e.g., polyethylene (PE) and polypropylene (PP), accounted for 63% of global plastic demand in 2019. [2] Their low recycling rate (below 5%) exacerbates the environmental threat. [1, 3-5] Mechanical recycling and incineration degrade the properties and emit significant greenhouse gas (GHG), respectively. [6-9] Catalytic deconstruction can mitigate these challenges toward a circular society. [10-13].

Hydrogenolysis is a promising catalytic technology for upcycling of PO.[14] Recent contributions over Pt [15–18] and Ru catalysts [19–25] demonstrated the feasibility of producing high-value fuels, waxes, and lubricants, at milder conditions (below 250 °C) than pyrolysis (360-550 °C). [26,27] Pt-based catalysts selectively produce fuels (C12 +) but are 1–2 orders of magnitude slower than Ru. [15–24] Ru raptures C-C bonds rapidly but produces methane of low value. For example, near stoichiometric conversion to methane was reported on a Ru/C catalyst at long space-time and/or high temperatures; [20,25] others reported < 10% yield. [21-23] Mechanistically, Nakaji et al. [22] attributed the high liquid yield (82%) in low-density PE (LDPE) to small Ru nanoparticles (<1.5 nm) on CeO₂, supported by their earlier work on squalane (C₃₀H₆₂) hydrogenolysis [28,29]. Chen et al. [30] observed reduced methane selectivity in PO hydrogenolysis on an ultra-low loading (<0.25%) Ru/CeO₂ due to higher coverage of adsorbed hydrogen on the sub-nm, cationic Ru. Jia et al. [24] found a significant reduction in gaseous products in high-density PE (HDPE) at elevated H₂ partial pressures over Ru/C catalysts due to prevalent internal C-C dissociation. Our previous work [21] on LDPE hydrogenolysis on Ru on tungstated zirconia (Ru-WZr) corroborates this dependence on hydrogen. More importantly, we demonstrated that highly dispersed sub-nm (WO_x)_n clusters could store and supply extra hydrogen to Ru via a reverse hydrogen spillover, which alleviates the hydrogen deficiency and suppresses methane formation. The ability of the oxide to increase the hydrogen storage and reduce the hydrogen pressure has significant ramifications on compressors' costs. Discovering catalysts with similar or improved performance is crucial.

In the present work, LDPE hydrogenolysis is examined under mild conditions. We synthesize and test a series of Ru on doped zirconia

https://doi.org/10.1016/j.apcatb.2022.121899

Received 3 June 2022; Received in revised form 20 August 2022; Accepted 23 August 2022 Available online 27 August 2022 0926-3373/© 2022 Elsevier B.V. All rights reserved.

^{*} Corresponding author at: Center for Plastics Innovation, University of Delaware, 221 Academy St., Newark, DE 19716, USA. E-mail address: vlachos@udel.edu (D.G. Vlachos).

catalysts (Ru-XZr, X = Ti, Nb, Ce, W, V, Mo, Fe; hereafter, the element refers to the corresponding oxide) to reveal principles for methane suppression. We use comprehensive characterization, theory, and surrogate molecules and discover an inverse volcano correlation between methane suppression and the reducibility of the dopant oxide and reveal two pathways producing methane whose relative importance depends on the hydrogen availability on the catalyst. Catalysts with intermediate reducible dopant oxides, such as W, V, and Mo, store and supply the most hydrogen via reverse spillover and are the most effective in methane suppression under H_2 -lean conditions.

2. Methods

2.1. Catalyst preparation

The doped zirconia (XZr, X = W, V, Mo, Nb, Ce, Ti, and Fe) supports were synthesized by impregnating dopant precursors (Table S1) into zirconium oxyhydroxide (ZrO_x(OH)_{4–2x}), which was prepared by hydrolyzing a zirconyl chloride octahydrate (ZrOCl₂ · 8 H₂O, Aldrich, 98%) solution using ammonium hydroxide (NH₄OH, Aldrich, 28–30 wt% in H₂O). Both solutions were added dropwise via peristaltic pumps into stirred water at a pH of 10. The resulting suspension was aged under vigorous stirring for 12 hr, followed by filtration and rinsing (aqueous NH₄OH solution at pH of 10) until Cl⁻ ions were absent. $ZrO_x(OH)_{4-2x}$ was dried at 110 °C in static air for 12 hr and was impregnated by the dopant precursors. The mixtures were dried at 110 °C for 12 hr and calcinated in static air for 3 hr (2 °C/min ramp) at 800 °C (WZr, MoZr, CeZr, and TiZr) or 650 °C (VZr, NbZr, and FeZr) to yield comparable surface areas. Nominal dopant loadings and other basic characteristics are tabulated in Table S3.

The doped-zirconia-supported ruthenium catalysts (Ru-XZr) were prepared using the successive incipient wetness impregnation method. Ruthenium (III) nitrosyl nitrate solution (Ru(NO)(NO₃)_x(OH)_{3-x}, Aldrich, 1.5 wt% Ru) was impregnated on the XZr supports to achieve 5 wt% nominal metal loading. They were dried at 110 °C for 12 hr and reduced at 250 °C for 2 hr in a tubular reactor using a 100-sccm, 10% H₂ in He flow. The reference catalysts, Ru supported on bare and W/Mo doped titania and silica (Ru-Ti, Ru-Si, Ru-WTi, Ru-WSi, Ru-MoTi, and Ru-MoSi), were prepared by similar procedures. TiO_x(OH)_{4-2x} was synthesized by precipitation using titanium(IV) isopropoxide (Ti[OCH (CH₃)₂]₄, Aldrich, 97%); titania was prepared by calcining TiO_x(OH)_{4-2x} at 450 °C; W/Mo doped silicas were prepared using amorphous fumed silica (175–225 m²/g) and were calcined at 800 °C. The nominal loadings of Ru and dopants are omitted for clarity.

2.2. Catalyst characterization

The BET surface area and porosity were measured using N₂ as the adsorbent at 77 K with a Micromeritics ASAP 2020 instrument. X-ray diffraction (XRD) patterns of powdered materials were measured using a Brucker D8 diffractometer equipped with a Cu Ka source. Raman spectra were acquired at ambient conditions using a Raman Spectrometer (HORIBA) equipped with a green line solid-state laser (532 nm). Air-free X-ray photoelectron spectroscopy (XPS) analysis spectra were collected using a Thermo Fisher K-Alpha Instrument equipped with an Al(K) X-ray source. The samples were pretreated in a tubular flow reactor in a 10% H₂ in He flow at 250 °C for 1 hr, cooled, and transferred in an XPS vacuum stage in a glove box ($P_{O2} < 1000$ ppm). Bright-field transmission electron microscopy (BF-TEM) images were acquired with a Field Emission Gun Transmission Electron Microscope (JEOL, JEM-2010 F), operated at 200 kV. Dark-field scanning transmission electron microscopy (DF-STEM) was performed with a JEOL NEOARM operating at 200 kV with detailed methodology published elsewhere. [21].

The apparent Ru dispersions were measured on a Micromeritics AutoChem II instrument using a H₂ titration method reported by Iglesia and coworkers. [31] Neither the reduction history of Ru nor the SMSI effect of the doping oxides influences the titration stoichiometry. Each sample was pretreated in-situ under 10% H₂ in Ar flow at 250 °C for 1 hr, purged in Ar flow for 1 hr at 250 °C, cooled, and kept at -73 °C (\pm 10 °C) using a liquid N₂-ethanol bath. The sample was then treated in a 1% O₂ in He mixture at -73 °C for 15 min, purged in Ar flow at -73 °C for 15 min, and then heated in Ar flow and stabilized at 100 °C for 1 hr. Ru dispersions were measured using H₂ pulsing titration of the surface ruthenium oxides at 100 °C.

Temperature Programmed Reduction (TPR) and Temperature Programmed Desorption of adsorbed hydrogen (H₂-TPD) were performed in a continuous flow reactor with online analysis using Mass Spectroscopy (MS) (Pfeiffer Vacuum Ominstar GSD 301 C quadrupole mass spectrometer). In a TPR experiment, the sample was purged in He at 250 °C for 1 hr and cooled down to room temperature. The gas was switched to a 60-sccm, 5% H₂ in He flow and was stabilized for at least 1 hr. TPR was then performed at a ramping rate of 10 °C/min from 27° to 1000°C. In a H₂-TPD experiment, the sample was reduced at 250 °C in a 60-sccm, 5% H₂ in He flow for 1 hr and cooled down to room temperature. The gas was switched to a 60-sccm pure He, purging the sample for 1 hr. The H₂-TPD was then performed at a ramping rate of 10 °C/min from 27° to 1000°C. All MS signals were normalized to He as an internal reference. Calibration was done using a MicroGC (990 MicroGC, Agilent) equipped with an MS5A column.

Diffuse reflectance IR spectra (DRIFTS) were acquired on a Nicolet 8700 spectrometer (Thermo Scientific) equipped with a liquid-nitrogencooled MCT detector. Powder samples were loaded in a heating holder located at the center of an environmentally controlled high-temperature cell (Harrick). The moisture in the feed was removed by a liquid nitrogen trap. To eliminate the interferences from water formation after H₂ exposure, all samples were pre-reduced in-situ at 350 °C for 1 hr in a 60-sccm, 10% H₂ in He flow, followed by a purge in 60-sccm He at 350 °C for 1 hr. Difference spectra were obtained at 250 °C by subtracting the reference spectrum collected in He from the steady-state spectrum taken in 10% H₂ in He flow at the same temperature.

2.3. Activity tests

2.3.1. Reactivity LDPE hydrogenolysis studies

Prior to reactions, all catalysts were reduced *ex-situ* in a 100-sccm, 10% H₂ in He flow at 250 °C for 1 hr (10 °C/min ramping rate). 2 g of low-density polyethylene (LDPE, M_w ~76 kDa) was mixed with 25–50 mg catalyst and added into a 50 mL stainless-steel Parr reactor with a 700 μ L stir bar. The reactor was sealed, purged with H₂ five times, and charged to 30 bar H₂ (standard temperature and pressure, STP). The reactor was heated up to 250 °C for 20 min, maintained at 250 °C for 2 hr under stirring, and quenched in a water/ice bath to below 10 °C before collecting gases, liquids, and solid residues.

2.3.2. n-hexane hydrogenolysis at 1 bar H_2

n-hexane (Aldrich, \geq 99%) hydrogenolysis was performed at 1 bar and 250 °C in a continuous flow reactor. It consisted of an 18-inch long, ¼-inch ID quartz tube placed vertically in a cylindrical furnace. The catalyst bed (typically 30 mg) was diluted 100 times using inert ZrO₂ and held in place by quartz-wool plugs and coarse quartz pellets loaded on both ends of the catalyst bed. The thermocouple was protected by a quartz sleeve inserted at the catalyst center, which was heated in the isothermal region of the furnace. Before rate measurements, the catalyst was pre-reduced in-situ at 250 °C for 1 hr in a 36-sccm, 10% H₂ in He flow. *n*-Hexane (0.025 bar) was introduced into the flow using a syringe pump (New Era Pump System) and mixed thoroughly with the flow before entering the reactor.

2.3.3. n-dodecane hydrogenolysis at high H₂ pressures

n-dodecane (Aldrich, \geq 99%) hydrogenolysis was performed in a continuous flow reactor at 20–60 bar H₂ and 250 °C. The reactor was a

stainless steel HPLC tube, 150-mm in length and 4.6-mm in inner diameter. It was placed horizontally in a heating jacket. The catalyst bed was held in place by quartz-wool plugs and coarse quartz pellets loaded on both ends, and inert rods were inserted to eliminate the free volume. The thermocouple measures the reactor wall temperature at the catalyst location. Before the rate measurements, the catalyst was pre-reduced insitu at 250 °C in a 30-sccm pure H₂ flow at 1 bar. The temperature was maintained at 250 °C, and the reactor was charged to 20–60 bar, regulated by a back-pressure regulator (Equilibar, U3L series). After the pressure was established, the liquid feed, a 0.05 mL/min *n*-dodecane, was introduced into the flow using an HPLC pump (Teledyne SSI, LS-class), mixed fully with the gas flow and sent into the reactor. The gas and liquid products were cooled to 10 °C before separation in a microcondenser (1 mL).

2.4. Product collection and analysis

Products from the gas-phase n-hexane hydrogenolysis reaction were analyzed online using FID gas chromatography (GC) equipped with an Agilent HP-Plot GC column. For n-dodecane and the LDPE hydrogenolysis reactions, gaseous products, typically C1-C6, were collected at 10 °C using a Tedlar bag and analyzed by the said GC-FID. Quantification was done using standard calibration mixtures. Soluble products from LDPE, typically C4 - C35, were extracted using a 20 mL dichloromethane (CH₂Cl₂, Fisher Scientific, ACS grade) with 20 mg *n*-octacosane external standard (n-C28, TCI chemicals, >98%). The soluble products were analyzed using GC-MS (Agilent, DB-1 column) for identification and GC-FID (Agilent, HP-1 column) for quantification. The liquid streams from n-dodecane hydrogenolysis, consisting of C4 - C11 alkanes, were dissolved into a calculated volume of the n-C28/CH2Cl2 solution and were analyzed using GC-FID (Agilent HP-1 column). Representative raw GC traces from the LDPE decomposition products are shown elsewhere. [21].

The yield of product alkanes with *i* carbons (C_i) was calculated using the following equation:

 $Y_i = \frac{n_i}{n_{minial}}$ where n_i is the moles of carbon in C_i, and $n_{initial}$ is the same in the initial LDPE feedstock. The mole-carbon selectivity (mol-C%) of product alkanes with *i* carbons (C_i) is evaluated from:

$$S^{molC}_{i} = \frac{Y_{i}}{\sum\limits_{non-solid} Y_{i}}$$

Here $\sum Y_i$ corresponds to the yield of non-solid products, namely, the combined yield of all *gaseous* and *soluble* liquid products.

In the high-pressure n-dodecane hydrogenolysis reaction, the moleproduct selectivity (mol-P%) was adopted to analyze C-C scission patterns. The mole-product selectivity of product alkanes with *i* carbons (C_i) is calculated from:

$$S^{molP}{}_i = \frac{i^{-1} \times n_i}{\sum\limits_{i=1-11}^{i=1-11} (i^{-1} \times n_i)}$$

In the gas-phase n-hexane hydrogenolysis reaction, the initial turnover frequency (TOF) was obtained by extrapolating the time-on-stream TOF values to t = 0. The TOF of hexane is calculated from:

 $TOF = \frac{r_{C6}}{m_{cat} \times d_{Ru}}$ where r_{C6} is the n-hexane consumption rate in mol/s, m_{cat} is the mass of catalyst in grams, and d_{Ru} is the Ru site density in mol/gram measured by low-temperature H₂/O₂ titration (Table S3).

2.5. Modelling

We performed density functional theory (DFT) calculations using the plane-wave-based Vienna ab initio simulation package (VASP), version 5.4.4. [32–34] The electron–electron exchange and correlation energies were computed using the Perdew, Burke, and Ernzerhof (PBE) functional with D3 dispersion corrections. [35,36] Core electrons were treated with the projector augmented-wave (PAW) pseudopotentials. [37,38] The metal oxides were simulated using the structures of the primitive cells. Initial structures along with GGA+U [39] values are

referenced to the Materials Project. [40] The formation enthalpy was calculated by subtracting the electronic energy of metal oxides from their elemental electronic energy contributions. The Brillouin zone was integrated using a $8 \times 8 \times 8$ k-mesh based on the Monkhorst–Pack method [41] with a Gaussian smearing factor of 0.1 eV. For the plane-wave set, a cutoff energy of 520 eV was used. Electronic structure calculations were performed iteratively, and electronic structures were converged when the difference in energy between subsequent steps fell below 10^{-6} eV. Geometries were optimized until the maximum of all forces fell below 0.02 eV/Å. Table S2 presents the unit cells and calculated formation enthalpies on a per-atom basis.

3. Results and discussion

We perform extensive characterization and correlate the results with catalyst performance to assess various hypotheses and expose the dominant mechanism of the promotion of dopants. We supplement the LDPE work with surrogate experiments.

3.1. LDPE hydrogenolysis on doped zirconia-supported ruthenium (Ru-XZr) catalysts

LDPE deconstruction was conducted over doped zirconia-supported ruthenium catalysts (Ru-XZr, X = W, V, Mo, Nb, Ce, Ti, and Fe). Catalysts loadings were adjusted to achieve similar non-solid yields (~70-80%) and compare product distributions. The Mo and V catalysts achieve (Fig. 1a-b) promotional deconstruction similar to W. Compared to the Ru-Zr catalyst (16% methane, 49% liquid [C₄-C₃₅]), [21] the W-, V-, and Mo-doped catalysts reduce the methane yields to 8.6%, 10%, and 9.2%, respectively (Fig. 1b) and improve liquid (C₄-C₃₅) yield (Fig. 1a) to 63%, 68%, and 65%, respectively, with heavier liquid distributions centered at C15 (Figure S1a). The Ti-, Nb-, and Ce-doped catalysts show minimal improvement compared to the Ru-Zr catalyst. They are prone to heavier methane production (Fig. 1d, 20%, 15%, and 15%, respectively). The liquid fractions decompose more aggressively to shorter alkanes (Figure S1b, centered at C11), although more or comparable solid residues remain (Fig. 1c, 21%, 26%, and 28%, respectively). W, V, and Mo yield more valuable fuels compared to Ti, Nb, and Ce (Fig. 1e, shaded boxes for average values): gasoline from 18% to 23%, jet fuel from 25% to 30%, diesel fuel from 35% to 43%, and wax/lubricant base-oil from 15% to 20%. The performance of the Ru-FeZr catalyst resides between the two groups, shown separately in Figure S2 for clarity. Next, we evaluate the possible origins of the promotional effect.

3.2. Effect of ruthenium particle size and catalyst reduction on hydrogenolysis

The Ru particle size can influence rates and selectivities in the hydrogenolysis of small alkanes and polymers [30, 42–45] when it changes over a broad range, e.g., 3 - 17 nm [42,43], 0.8 - 9 nm [44] or $2.5 \times 10^{-4} - 0.72$ in H/Ru dispersion [45]. Chen et al. recently reported high PO decomposition rates and low methane over sub-nm range Ru (0.8 ± 0.2 nm). [30] The particle size effect above 0.5 wt% Ru loading (>1.3 nm) was slight. The current work utilizes high (5 wt%) Ru loading. The Ru particle sizes on select (Mo, Nb, and Fe) catalysts are similar, 2–3 nm on average (Fig. 2). The small sizes corroborate the Ru dispersions measured by low-temperature O_2/H_2 titration (Table S3) and the absence of Ru XRD pattern (Figure S3).

We selected the Ru-MoZr catalyst for further studies. High magnification TEM (Fig. 2a-b), high-angle annular dark-field (HAADF) STEM, and energy dispersive spectroscopy (EDS) elemental mapping (Figure S4) of the catalyst pre-reduced at 250 °C show $\sim 1 - 4$ nm Ru nanoparticles with an average size of 2.0 nm (Figure S5d). Similar to Ru-WZr, [21] the strong metal-support interaction (SMSI) of Ru with the Mo oxide reduces the exposed Ru site density (60 µmol/g, Table S3) compared to Ru-Zr [21] and other Ru-XZr catalysts. Pre-reduction at



Fig. 1. *Effect of doping oxide in doped zirconia supported ruthenium catalysts (Ru-XZr) on LDPE hydrogenolysis.* (**a**, **c**) Carbon balance (grey dots), yields of soluble (solid bars), and gaseous (faded bars) products; (**b**, **d**) Detailed carbon distributions of C1–3 products; **e**, Yields by fuel range, Gasoline: C5-C12, Jet Fuel: C8-C16, Diesel: C9-C22, and Waxes/Lubricant base-oils: C20-C35. Data error bars shown for selected catalysts are indicative of this work. Reactions performed at 250 °C, 50 bar H₂, 2 hr, 2 g LDPE; 50 mg of Ru-WZr and Ru-MoZr catalysts, and 25 mg loading for the rest.

400 °C further lowers the Ru site density to 9 µmol/g (Table S4) due to a slight increase in Ru particle size from 2.0 to 2.5 nm (Figure S5d-e) and a higher SMSI coverage commonly seen at higher reduction temperatures. [46,47] Despite these changes, the LDPE hydrogenolysis on the pre-reduced (at 250 °C and 400 °C) catalysts shows no observable difference in product distribution at a similar plastic conversion (Figure S5a-c). The longer space time (6x, defined as reaction time / LDPE-to-catalyst mass ratio, Table S4) required on the 400 °C pre-reduced catalyst to reach a similar conversion (~40%) correlates with the 6x decrease in the Ru site density (Table S4), suggesting that the turnover frequency (TOF) is similar. These results indicate that neither the Ru particle/domain size nor any possible changes in the electronic and geometric structure of Ru induced by the MoO_x/Ru SMSI encapsulation describes the promotional effect of the dopant. Furthermore, the overall rate of the bifunctional catalyst in converting the LDPE is controlled by the metal chemistry.

3.3. Effect of textural properties of ZrO₂ and support

The crystal structure of the zirconia support varies with the dopant, as shown in the XRD patterns and Raman spectra (Figure S6). While TiZr and VZr are predominantly monoclinic, the rest are primarily tetragonal (Figure S6). However, the crystal phase does not appear to correlate with the catalytic performance of the catalysts. The Brønsted acidity on some XZr supports, such as WZr, can promote C-C cracking and isomerization of plastics. [48,49] However, we have shown previously that the degree of product branching on Ru-WZr and Ru-Zr catalysts is invariant, [50] indicating the absence of acid-catalyzed reactions. The key difference of Ru-WZr from the hydrocracking-hydroisomerization Pt-WZr catalyst we reported previously [48,49] is that Ru tends to undergo deep dehydrogenation/rapid C-C scission rather than form olefinic intermediates critical to the acid-catalyzed pathways.

N₂-BET analysis indicates that W, Mo, and V catalysts possess higher

surface area and smaller pore size than the rest (Table S3). However, the poor selectivities (Figure S7a-c) of high-surface-area Ru-WSi and Ru-MoSi catalysts (\sim 150 m²/g) suggest that high surface areas alone do not give good performance. The promotional effect of W and Mo on ZrO₂ does not translate to SiO₂. The performance of the SiO₂-supported catalysts (Figure S7a-c) hints at the importance of the support and the dopant surface species because Mo and W oxides tend to aggregate to large crystalline domains on SiO₂, [51,52] potentially weakening the promotional effect. On the other hand, the promotional effect extends beyond zirconia to other supports, such as TiO₂, as discussed below (Figure S7d-f).

3.4. Effect of dopant oxides

Next, we explore possible correlations between dopant structures and catalytic performance. Ce and Ti dopants interact weakly with the ZrO₂ support: the dopant and the support aggregate, resulting in low surface area materials but high averaged dopant surface densities ($\#_{dopant}/nm_{ZrO_2}^2$) (Table S3). XRD and Raman spectra of TiZr show anatase TiO₂ features, suggesting separation from the monoclinic ZrO₂ support (Figure S6a, c). It is difficult to distinguish cubic CeO₂ (or CeZrO mixed oxides) from tetragonal ZrO₂ by XRD due to the overlapping patterns. Raman bands at 144, 265, 315, 463, and 642 cm⁻¹ are consistent with tetragonal ZrO₂. The extra shoulder at 473 cm⁻¹ is assigned to CeO₂ or CeZrO mixed oxides surface species in fluoride cubic structure (Figure S6a, c). [53].

The promotional dopants show unique structural characteristics. TEM, HAADF-STEM images, and EDS mapping of the Ru-MoZr catalyst (Fig. 2a-b and Figure S4) exhibit highly dispersed sub-nm (MoO_x)_n clusters on ZrO₂ that closely resemble (WO_x)_n clusters.^[21] The Raman spectra on W-, Mo-, and V-doped ZrO₂ show characteristic bands at ~700 – 900 cm⁻¹ (ν (M-O-M), broad feature) and ~950 – 1000 cm⁻¹ (ν (M=O), sharp feature) (Figure S6b), suggesting highly dispersed and

C. Wang et al.

Applied Catalysis B: Environmental 319 (2022) 121899



Fig. 2. . Bright-field TEM (BF-TEM) images of select Ru-XZr catalysts. a-b, Ru-MoZr with Ru nanoparticles mostly between 1 and 4 nm and high magnification of a \sim 3 nm Ru hemispherical nanoparticle (green arrow), and a rough surface layer consisting of sub-nm (MoO_x)_n clusters (orange arrow); **c-d**, Ru-FeZr with a ZrO₂ grain with one side (blue arrow) loaded with Ru and/or FeO_x nanoparticles and another smooth and clean side (red arrow) and high magnification of two \sim 2–3 nm particles (orange and green arrows) with distinct color contrast and lattice features; **e-f**, Ru-NbZr catalysts with Ru nanoparticles mostly of 1–4 nm and high magnification of a \sim 3 nm Ru hemispherical nanoparticle (green arrow), and a rough surface layer consisting of sub-nm (NbO_x)_n clusters (orange arrow).

distorted dopant oxides, consistent with the absence of XRD patterns (Figure S6a). The dopants form near-monolayer [54–56] nominal coverages at a surface density of ~7, 5, and 5 nm⁻², respectively (Table S3), due to strongly wetting the ZrO₂ support.[57] TiO₂ is also known to well disperse MoO_x and WO_x. [58–61] Ru-MoTi and Ru-WTi catalysts produce much lower methane than Ru-Ti (Figure S7d-f), confirming the strong correlation between low methane formation and high dopant dispersions. Excitingly, in comparison to polypropylene deconstruction over Ru/TiO₂, [23] specific dopants provide an excellent means of reducing methane.

However, high dopant dispersions are not sufficient for promotion, as exemplified by the non-promotional Nb and Fe catalysts. TEM images of Ru-NbZr show highly dispersed (NbO_x)_n species on the ZrO₂ support (Fig. 2e-f), similar to the (MoO_x)_n (Fig. 2a-b) and (WO_x)_n clusters [21]; Ru-FeZr forms small FeO_x nanoparticles similar to Ru (Fig. 2c-d, distinguished by lattice spacing). XRD of NbZr and FeZr show the absence of bulk NbO_x or FeO_x; ZrO₂ is in the metastable tetragonal phase (Figure S6a). The broad Raman band at ~800 cm⁻¹ (Figure S6c) was previously assigned to mixed ν (Nb-O-Nb) modes of distorted, corner-sharing, and dispersed species. [62] The 670 cm⁻¹ band on FeZr is consistent with Fe₃O₄ nanoparticles. [63].

3.5. Role of hydrogen

Results discussed next demonstrate that promotional catalysts can uptake, store, and supply additional amounts of hydrogen at reactionrelevant conditions, which we correlate with methane suppression. TPR-MS on select Ru-XZr catalysts (X = Nb, Mo, and Fe) (Fig. 3) referenced to XZr (Ru-free) catalyst demonstrate hydrogen spillover. NbZr shows a slight reduction (0.4 mmol H₂/g) at temperatures exceeding 650 °C (Fig. 3a), suggesting low reducibility of NbO_x. This feature is lowered by 200 °C on Ru-NbZr, but is still high to interfere with the low-temperature LDPE hydrogenolysis. The Ru-NbZr consumes ~0.5 mmol H₂/g below 250 °C (Fig. 3a), primarily due to the reduction of RuO_x, consistent with the Ru-Zr data (~0.6 mmol H₂/g) [21]. Air-free XPS results corroborate the lack of reduction of NbO_x and the substantial reduction of RuO_x at reaction conditions (Figure S9a-c).

TPR-MS of MoZr shows features at 450 °C and 720 °C (Fig. 3b), assigned to the reduction of Mo⁶⁺ to Mo⁴⁺ and Mo⁴⁺ to Mo⁰, respectively, [64] suggesting higher reducibility than NbZr. These features decrease substantially on Ru-MoZr with less H₂ uptake above 300 °C. However, the low-temperature, sharp feature is substantially larger, ~1.3 mmol H₂/g (Fig. 3b), > 2x higher than Ru-Zr or Ru-NbZr. The extra hydrogen uptake occurs through spillover from Ru to MoO_x, similar to Ru-WZr as the oxide does not dissociate H₂. [21] A significant fraction of additional hydrogen likely remains on the catalyst up to 250 °C because the formation of H₂O is similar on Ru-MoZr and Ru-NbZr (Figure S8a-b). Air-free XPS of the reduced Ru-MoZr indicates a reduction of the Mo⁶⁺ centers, evidenced by the additional Mo3d doublet at 231.5 and 234.8 eV. The degree of Mo⁶⁺-to-Mo⁵⁺ reduction is more significant than WO_x, [21] consistent with the reduction ranking indicated by the calculated oxide formation enthalpy (Table S3).

TPR-MS of FeZr lights off at 190 °C, roughly 160 °C below MoZr (Fig. 3c), suggesting higher reducibility. The two features at \sim 380 °C and 730 °C correspond to reductions of Fe³⁺ to Fe²⁺ and Fe²⁺ to Fe⁰, respectively. [65] The presence of Ru substantially decreases the



Fig. 3. . Doping oxide reducibility and hydrogen spillover on Ru-XZr catalysts. a-c, TPR-MS (positive features, m/z = 2) measurements on Ru-loaded (solid curve) and Ru-free (faded curve) over NbZr (orange), MoZr (purple), and FeZr (brown) catalysts; **d-e**, H₂-TPD-MS (m/z = 2, normalized by N₂ carrier at m/z = 28) measurements on Ru-XZr catalysts (X = W, V, Mo, Nb, Ce, and Fe); **f-g**, Difference DRIFTS spectra of Ru-XZr catalysts (X = W, Mo, and Nb) collected at 250 °C upon exposed to steady-state 10% H₂ flow carried by 60-sccm He; bending (**f**) and stretching (**g**) vibration regimes of O-H groups. Difference spectra were obtained by subtracting the absorbance spectra collected prior to H₂ exposure from the spectra post-H₂ exposure at 250 °C.

reduction temperature of FeO_{x} , indicating hydrogen spillover and subsequent oxide reduction, as found by density functional theory and microkinetic simulations. [66] The low-temperature H₂ uptake feature is broad, indicating bulk reduction for Ru and Fe oxides. The high-temperature feature disappears completely, suggesting a near-complete reduction to metallic Fe at LDPE reaction temperatures.

 H_2 -TPD-MS measurements highlight the potential of the Ru-XZr catalysts to serve as reservoirs of hydrogen. The data (Fig. 3d-e)

indicates broader desorption profiles than Ru-Zr [21] (dashed line) due to hydrogen spilling over on reducible oxides and being released at high temperatures. [67] Although greater in amount (Table S5), hydrogen desorbed at $> 250 \ ^\circ\text{C}$ should not interact with the LDPE reaction. Conversely, the amount of low-temperature hydrogen desorption below 250 °C (Table S5), which is directly relevant to the reactions, correlates well with methane suppression. We further elaborate on the implications of this correlation in the next section. Since we have examined and precluded other possible factors, such as Ru particle size, SMSI effect, acidity, and the support's textural properties, the TPR and H2-TPD measurements together led us to a likely explanation for the observed methane suppression: Promotional catalysts store and desorb more H₂ than Ru-Zr and non-promotional Ru-XZr catalysts (Fig. 3d-e). This hydrogen is mobile and reactive under reaction conditions and facilitates the hydrogenation of alkyls on the Ru surface, followed by the desorption of alkanes. This prevents over-dehydrogenation and sequential C-C bond scission leading to methane. We note that the amounts of H₂ desorption do not necessarily match the Ru site density measured by low-temperature H_{2/O2} titration due to spillover. For example, the Ru site densities of the W and Mo catalysts (76 and 60 µmol/g, respectively, Table S3) are only half of that of the Ru-Zr and Ru-Ce catalysts (123 and 118 μ mol/g, respectively), [21] the extra H₂ desorbed at low temperatures is attributed to the hydrogen storage.

In-situ DRIFTS measurements were performed on select Ru-XZr catalysts (X = W, Mo, and Nb) to identify surface hydrogens on the dopant oxides. Difference absorbance spectra were obtained by subtracting the spectra collected before and after H₂ exposure at 250 °C. The samples were pre-reduced in H₂ and purged in He at 400 °C to eliminate the interference of adsorbed hydrogen or water (details reported elsewhere [21]). Upon H₂ exposure at 250 °C, the difference absorbance associated with the Ru-WZr catalyst shows three distinctive bands at \sim 1600, 1418, and 1220 cm^{-1} in the $\delta(\text{OH})$ regime (Fig. 3f), consistent with transmission FTIR data. [21] The 1600 cm⁻¹ feature was assigned to water-like surface species that release molecular H2 upon heating or evacuation; [68] the latter two were assigned to δ (OH) modes of W-OH interacting with adjacent O atoms. The corresponding $\nu(OH)$ modes exhibit broad features around $\sim 3000 \text{ cm}^{-1}$ due to H-bonding (Fig. 3g). The Ru-MoZr catalyst exhibits similar $\delta(OH)$ and $\nu(OH)$ modes. The less stable [21] $\delta(OH)$ band at 1418 cm^{-1} is absent at 250 $^\circ C$ due to the higher reducibility of MoOx than WOx. Conversely, the Ru-NbZr catalyst shows a negligible difference feature associated with $\delta(OH)$ or $\nu(OH)$

modes when exposed to H_2 at 250 °C. No additional hydrogen can be supplied to Ru from NbO_x, leading to no promotional effect.

3.6. Mechanistic insights using surrogates

We have previously shown that the LDPE hydrogenolysis over Ru-WZr catalyst runs at H₂-lean conditions, evidenced by a positive reaction order of H₂, [21] consistent with the literature. [30] Additional hydrogen stored on Ru-WZr can suppress methane because it enhances hydrogenation of surface alkyls and reduces secondary, methane-forming C-C scissions.

The processing times (0.025–0.05 hr· g_{cat} g_{LDPE}^{-1}) on various Ru-XZr catalysts for similar LDPE conversions (Fig. 1) correlate inversely with the corresponding Ru site density (Table S3), suggesting that the rate of deconstruction is independent of the dopant. Since the TOF of a polymer mix cannot be defined readily, we perform n-hexane hydrogenolysis at 250 °C and 1 bar H₂ to represent LDPE hydrogenolysis at H₂-lean conditions.[21] This surrogate is adequate for our purpose because both reactions exhibit positive reaction orders to hydrogen; [21] the CH₄ formation rates (Fig. 4a) and the turnover frequency of C-C scission per Ru site (Ru-VZr as an example, $\sim 3.5 \text{ s}^{-1}$ [C₆H₁₄] vs. 1.2 s⁻¹ [LDPE]) are also of similar magnitude. The initial TOFs (per-Ru-site) of n-hexane across all Ru-XZr catalysts are nearly identical (Fig. 4a), suggesting that dopants do not modify the Ru-catalyzed C-C breaking events. In contrast, the methane formation rates from both LDPE and hexane clearly depend on the dopants (Fig. 4a). The dopant-independent hexane TOF combined with the dopant-affected methane formation rates suggest that the dopants only influence the fragments in each hexane turnover.

Since the dopant reducibility is implicated according to hydrogen sorption (Fig. 3a-e), we plot in Fig. 4b the methane selectivity in both LDPE and *n*-hexane hydrogenolysis and the capacities of reactionrelevant hydrogen storage on the dopant oxides (Table S5, defined as the amount of low-temperature (<250 °C) hydrogen desorption by H₂-TPD) against the standard formation enthalpy of oxides (Table S3), a descriptor for oxide reducibility. The methane selectivity displays an inverse volcano vs. the oxide reducibility for LDPE and n-hexane reactions, both indicating that only mildly reducible dopant oxides (W, V, and Mo) reduce methane formation. This coincides with the volcano correlation of hydrogen storage capacity vs. the oxide reducibility, indicating strong correlation between methane suppression and



Fig. 4. . Correlation between catalytic performance and dopant properties. a, "Per-Ru-site" methane formation rate for LDPE (grey) and n-hexane (blue) hydrogenolysis, and initial turnover frequency (TOF, red) for an ambient-pressure surrogate n-hexane hydrogenolysis over Ru-XZr catalysts (X = W, V, Mo, Ce, Nb, Ti, and Fe); b, Methane selectivity for LDPE hydrogenolysis and the ambient-pressure surrogate n-hexane hydrogenolysis and reaction relevant hydrogen storage on the dopant oxides as a function of the standard formation enthalpy of the doping oxide. LDPE reactions are shown in Fig. 1 and Fig. S2; The ambient-pressure surrogate n-hexane hydrogenolysis was performed at 250 °C, $P_{tot} = 1$ bar, $P_{H2} = 0.9$ bar $P_{C6} = 0.025$ bar, He makeup; WHSV ≈ 690 hr⁻¹; conversion < 5%.

hydrogen storage on mildly reducible oxides. Indeed, non-reducible oxides (e.g., Ti, Nb, and Ce) cannot store and supply additional hydrogen at reaction-relevant conditions, whereas over-reducible oxides (e.g., Fe) facilely react with hydrogen to produce water (Fig. 3).

Dodecane (C12, hereafter, Cx denotes n-alkane products with x carbons) hydrogenolysis was also performed at 250 °C and 20–60 bar H₂ on Ru-Zr and Ru-MoZr catalysts to identify the methane-producing pathways and their dependence on hydrogen availability. Secondary reactions are negligible in the kinetic regime (conversion <7%). Molar product (mol-P%) selectivity is used to showcase distributions of primary products, which are indicative of the locations of C-C scission.

A representative product distribution on Ru-MoZr catalyst at 60 bar H₂ (Fig. 5a) is nearly symmetric except for C1 and C11, suggesting one C-C scission per C12 turnover except for those producing methane. The C2–10 distribution is nearly uniform, suggesting that all internal C-C scissions are equiprobable. The C11 selectivity is \sim 3x the internal cracking products (C2–10), suggesting that direct terminal C-C scission is 3x more probable than the internal ones. Methane selectivity (42 mol-P%) is higher than C11 (15 mol-P%), indicating a second methane-producing pathway parallel to the primary terminal C-C bond scission. The excess methane does not pair with other products,

suggesting that it is a secondary product from the primary ones (C2–11) within the same C12 turnover. The slightly tilted distribution of C2-10 (inset, Fig. 5a) suggests that the secondary methane is more likely produced from the longer chains, because of their longer residence time on the Ru surfaces due to their higher heats of adsorption. A proposed reaction network is presented in Scheme 1. Dehydrogenation Rii of adsorbed alkane occurs on both terminal and internal C-C bonds, followed by the first C-C bond scission Riii, preferably on terminal carbons. The two resulting surface alkyls may be hydrogenated and desorb without further reaction Riv, giving methane via direct terminal scission. Alternatively, at least one of the two alkyls stays on Ru and undergoes further dehydrogenation and C-C scissions Rv. Demethylation is dominant due to the binding configuration Riii on the terminal carbon. In this sequential cracking path, several methane molecules are produced in a cascade until the surface alkyls are hydrogenated and desorb from the Ru surface via Rv.

The results of C12 hydrogenolysis at 20 - 60 bar H₂ over the Ru-MoZr catalyst, compared to its non-promoted Ru-Zr counterpart, are shown in Fig. 5b. At 60 bar H₂, the product distributions over the two catalysts are nearly the same (Figure S10), suggesting a lack of dopant effect. This is because sufficient H₂ on Ru ensures fast hydrogenation/ desorption (Riv, Scheme 1). At lower pressures, Ru-Zr produces more



Fig. 5. Effect of hydrogen pressure on the hydrogenolysis of n-dodecane. a, Selectivity over Ru-MoZr at 250 °C, 60 bar H₂, catalyst of 20 mg, H₂ and dodecane flow rates at 30 sccm and 0.05 mL/min, respectively, conversion = 3.6%. b, Selectivities over Ru-MoZr (purple) and Ru-Zr (orange) catalysts at 250 °C, catalyst of 20 mg, and H₂ and dodecane flow rates at 30 sccm and 0.05 mL/min, respectively. c, Hydrogen pressure dependence on the probability of terminal C-C bond scission over all direct C-C scission events (τ), and ratio between methane produced from the cascade and terminal C-C scissions (ϕ) over Ru-MoZr (purple) and Ru-Zr (orange) catalysts. d, Hydrogen pressure dependence on dodecane turnover rate and number of C-C scissions per dodecane turnover on Ru-MoZr (purple) and Ru-Zr (orange) catalysts. Reactions performed at 250 °C, 20–60 bar H₂, catalyst of 20 mg, H₂, and dodecane flow rates at 30 sccm and 0.05 mL/min, respectively.



Scheme 1. Schematic of the mechanism for LDPE hydrogenolysis.

methane and is more sensitive to pressure. At 20 bar H_2 , the methane selectivity on Ru-Zr is 60 mol-P%, 18% higher than at 60 bar. In contrast, Ru-MoZr catalyst has 48 mol-P % at 20 bar, increased by 6% only from 60 bar. These results clearly show that Ru-MoZr suppresses methane under H_2 -lean conditions.

Two quantities of interest, τ , and φ , are introduced to probe further the hydrogen effect on the methane-producing pathways and the roles of dopants. τ is the probability of direct terminal C-C bond scission over all primary C-C scissions (Riv, Scheme 1) and φ is the ratio of methane produced via the cascade (Rv) over the direct terminal C-C scission (Riv). Fig. 5c plots their dependence on hydrogen pressure over the Ru-MoZr and Ru-Zr catalysts. The two catalysts have similar τ values, suggesting that the dopant does not influence the location of the primary C-C scission, and thus, the hydrogen availability does not affect the likelihood of terminal vs. internal primary scissions. On the contrary, φ for both catalysts decreases sharply with increasing H₂ pressure due to suppressing the cascade methane-producing pathway. At 20 bar H₂, on Ru-Zr, methane is predominantly produced through the cascade pathway (Rv) (φ ~5); on Ru-MoZr φ is considerably lower but still high (3.2). φ drops quickly and becomes similar for both catalysts at higher pressures, emphasizing the absence of dopant effects in H₂-rich conditions. The hydrogen abundance is also evident from the near-zero reaction order of H₂ at low pressures that turns negative at high pressures (Fig. 5d). The numbers of C-C scissions per C12 turnover (Fig. 5d) correlate negatively with hydrogen pressure and are similar (~1.5) on both catalysts at 60 bar H₂. At 20 bar, the Ru-Zr catalyst breaks ~2.4 C-C bonds per C12 turnover, ~1.4 of which are from the methane-producing, secondary scissions (step Rv, Scheme 1), compared to a single scission from the cascade pathway on the Ru-MoZr catalysts.

The reaction orders of hydrogen in LDPE hydrogenolysis in this work (and most other hydrogenolysis schemes) are positive,[21] indicating that methane is predominately produced via secondary cascade C-C scissions. The proposed dopant effect is depicted in Scheme 2. The primary C-C scission is initiated following adsorption and dehydrogenation. The promotional dopants, such as Mo, can store and provide additional hydrogen via reversible spillover to supplement hydrogen supply at lean conditions and suppresses methane produced by a cascade C-C bond scission pathway by enhancing hydrogenation of the surface



Scheme 2. Schematic illustration of the methane suppression effect of the dopants.

alkyls.

A simple kinetic model for the proposed reaction mechanism (Scheme) is presented in the *Supplementary Information*. This model predicts a sufficient criterion for the hydrogen storage mechanism to increase the hydrogen coverage on Ru to be:

$$\frac{k_s}{2} \bullet \sqrt{K_A[A]} \bullet \frac{1}{k_H[H_2]} \bullet \frac{[H^{\#}]}{K_{\#}[\#]} > 1$$

Here k_s and k_H are the rate constants of surface reaction and hydrogen dissociation; K_A and K are the equilibrium constants of alkane dissociative adsorption and hydrogen spillover; [A] and $[H_2]$ are the partial pressures of alkane and hydrogen; and [H] and [] are the coverages of hydrogen and vacant sites on the dopants. Since this model assumes the surface reaction to be rate limiting (a slow step), this criterion intuitively requires (1) the polymer melt wetting the Ru surface covers most sites (large $\sqrt{K_A[A]}$); (2) a limited hydrogen availability on Ru from the gas (low $k_H[H_2]$); and (3) a high H storage and fast reverse spillover on favorable dopants (large $\frac{|H|}{K_{\parallel}}$). These predictions are qualitatively consistent with the reactivity and sorption experimental results, which demonstrated H-lean conditions for LDPE hydrogenolysis and abundant and facile reversible hydrogen spillover on promotional dopants.

We also derive from the simple kinetic model (see *Supplementary Information*) the methane selectivity expression for many turnovers:

$$S_{Me}^{total} = 1 - \left[\left(\frac{\alpha}{(1 - [H^*]) + \alpha} \right)^{TOF} \right]^{t}; \alpha = \frac{k_D}{k_{cas}} \times K_A[A]$$

Here $[H^*]$ is the hydrogen coverage on the Ru surface; *t* is the reaction time; k_D and k_{cas} are the rate constants of the direct recombinative desorption (*Riv*, Scheme 1) and the cascade (*Rv*, Scheme 1) pathways. This expression reconciles our experimental data, indicating that the methane suppression correlates strongly with an excess hydrogen coverage [H^{*}] on Ru via the hydrogen storage mechanism.

3.7. Discussion

Ru-based catalysts are very active for PO hydrogenolysis compared to other noble metals but also produce copious fractions of methane. The quest for developing Ru-based active and non-methane-producing catalysts has been growing. Our previous findings on the Ru-WZr catalyst [21] have shown that the (WO_x)_n domains serve as reservoirs for storing and supplying extra hydrogen via reversible hydrogen spillover under H₂-surface lean conditions (Scheme 2). Different from the (WO_x)_n domains on Pt-WZr [48] that serve as Bronsted acid centers in an adhesive mechanism, those on Ru-WZr hold extra hydrogen, which avoids the over dehydrogenation of alkyl species and C-C bond scissions (from deep dehydrogenated species) that produce methane. To further assess this hypothesis and explore other materials, we synthesized and characterized a series of Ru-XZr, X = Ti, Nb, Ce, W, V, Mo, Fe, catalysts. We found that similar to W, V, and Mo promote the selectivity to liquid fuels compared to the undoped RuZr catalyst but Nb, Ce, and Fe do not. Through small surrogate molecule experiments, we found a strong correlation between methane formation rate and the reducibility of the dopant exhibiting an inverse volcano curve. Only oxides that have moderate reducibility store sufficient hydrogen to avoid over-hydrogenation and minimize methane formation. The high decomposition activity at mild conditions (250 °C and 50 bar H₂) and short processing times (0.025–0.05 hr $g_{cat} g_{LDPE}^{-1}$) are remarkable and among the best. [14] Our data also supports that neither Ru particle size nor the ZrO₂ support is the key factor; rather, mildly reducible oxides suppress the methane formation.

The findings of this work reconcile previous literature on hydrogen partial pressure. Due to blocking the surface sites with macromolecules, even 50 bar H_2 results in H-surface lean conditions. The surface coverage results from the interplay of pressure, temperature [20,69],

substrate (size [70], degree of branching [30], etc.), and catalyst [30,71] (metal type, particle size, etc.). For instance, we showed previously that the reaction order of hydrogen for LDPE (~76 kDa) hydrogenolysis at 250 °C is positive from 50 to 130 bar H₂. [21] Chen et al. [30] observed more positive hydrogen reaction order on 2 wt% Ru/CeO2 than on 0.125 wt% Ru/CeO2 catalysts, and more positive with LDPE than polypropylene (PP). Rorrer et al. [20] for LDPE hydrogenolysis on a Ru/C catalyst showed 100% methane yield at 523 K and 30 bar H₂ and 35% at 473 K. They observed positive H_2 reaction order at 250 °C and 15-30 bar H₂ even with ultralow-Mw LDPE (4 kDa). With high-Mw PP (340 kDa), methane suppression was evident from 40 to 50 bar, suggesting that hydrogen on the surface was insufficient. Nakaji et al. observed > 0th order to hydrogen up to 60 bar on Ru/CeO₂ even with ultralow-Mw LDPE (4 kDa) at 513 K. Unlike Ru, Pt-based catalysts exhibit negative reaction order to hydrogen even at 100 psi, producing no methane even at 573 K, [16,17,72] owing to the weak dissociation of hydrocarbons relative to hydrogen. However, the activity on Pt is considerably lower than Ru due to the same reason. The change in the dominant cracking pathway with hydrogen partial pressure under hydrogen-lean conditions is consistent with microkinetic flux analysis we performed on ethane hydrogenolysis on Pt several years ago (see Figures 7 and 8 in Ref. [73] for a change of cracking from CHCH₃ at lower hydrogen pressures to CH₂CH₃ at higher pressures).

Nearly all active PO hydrogenolysis exhibit positive H_2 order and produce too much methane. Understanding the methane-producing mechanisms and their dependence on hydrogen availability is important. Previous works have correlated methane selectivity and hydrogen abundance. [24,30] However, the high methane fractions at low H_2 pressures (or low H coverage) were attributed to regioselectivity, namely higher ratios of terminal-to-internal C-C scission. The C12 surrogate reaction experiments showed that this route is rather minimal, although terminal C-C scissions are indeed more favorable. The alternative route of the cascade, in fact, dominates, especially under lean hydrogen, which has not been reported previously in PO hydrogenolysis.

Both the experimental and kinetics modeling results indicates that the additional hydrogen promotes the hydrogenation of surface alkyls, alleviating repeated methane formation along the cascade (Rv, Scheme 1). Conceptually, all means altering the competitive adsorption of hydrogen and hydrocarbons (i.e., hydrogen coverage on Ru) can tune methane selectivity. This can be achieved by varying temperature (endoand exothermicity of alkane and hydrogen, respectively) and partial pressure but also using sub-nm range Ru clusters to increase the coverage of adsorbed hydrogen, resulting in less methane. [30] Redox history also modifies H_2 chemisorption equilibrium on Ru, varying methane selectivity. [71,74] This work evidently demonstrates a general strategy and mechanism toward low-methane hydrogenolysis of LDPE beyond the impact of the hydrogen storage mechanism on promotional dopants.

4. Conclusions

This work examined LDPE hydrogenolysis over Ru on doped zirconia catalysts (Ru-XZr, X = Ti, Nb, Ce, W, V, Mo, Fe) under mild conditions to expose guidelines for methane suppression. Using surrogate hydrogenolysis reactions, we discovered an inverse volcano correlation between methane suppression and the reducibility of dopant oxides; catalysts with intermediate reducible dopant oxides, such as W, V, and Mo, are the most effective. Methane is produced by a direct terminal C-C scission or a cascade of consecutive C-C bond scissions, and the relative importance depends strongly on the hydrogen availability. Promotional catalysts store and supply additional hydrogen via spillover to minimize the methane-producing cascade pathway suppressing methane under H_2 -lean conditions.

CRediT authorship contribution statement

Cong Wang: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Kewei Yu, Boris Sheludko, Tianjun Xie, and Pawan Kumar:** Methodology, Investigation, Formal analysis. **Pavel A. Kots and Brandon C. Vance:** Investigation, Formal analysis, Writing – review & editing. **Weiqing Zheng:** Investigation, Formal analysis, Writing – review & editing, Supervision, Funding acquisition. **Eric A. Stach:** Writing – review & editing, Supervision, Funding acquisition. **Dionisios G. Vlachos:** Conceptualization, Writing – review & editing, Project administration, Funding acquisition.

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

Data in Brief is uploaded.

Acknowledgments

This work was supported as part of the Center for Plastics Innovation, an Energy Frontier Research Center funded by the US Dept. of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-SC0021166. The STEM and EDS elemental mapping were performed at the Singh Center for Nanotechnology at the University of Pennsylvania, a member of the National Nanotechnology Coordinated Infrastructure (NNCI) network, which is supported by the National Science Foundation (Grant NNCI-1542153). The authors gratefully acknowledge the use of facilities and instrumentation supported by NSF through the University of Pennsylvania Materials Research Science and Engineering Center (MRSEC) (DMR-1720530). The computational work used the Extreme Science and Engineering Discovery Environment (XSEDE), grant number PHY210032. XSEDE is supported by the National Science Foundation.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2022.121899.

References

- R. Geyer, J.R. Jambeck, K.L. Law, Production, use, and fate of all plastics ever made, Sci. Adv. 3 (2017), e1700782.
- [2] A. Chitalia, Why polyolefins are the polymers to watch, Wood Mackenzie (2020).[3] OECD, Improving plastics management: trends, policy responses, and the role of
- international co-operation and trade, Environ. Policy Pap. 12 (2018) 20. [4] U.S.E.P. Agency, Advancing Sustainable Materials Management: Facts and
- Figures Report, (2020). [5] G.G.N. Thushari, J.D.M. Senevirathna, Plastic pollution in the marine environment, Helivon 6 (2020), e04709.
- [6] A. Rahimi, J.M. García, Chemical recycling of waste plastics for new materials production, Nat. Rev. Chem. 1 (2017) 0046.
- [7] N. Ágnes, K. Rajmund, The environmental impact of plastic waste incineration, AARMS–Academic and Applied Research in Military and Public, Manag. Sci. 15 (2016) 231–237.
- [8] O. Eriksson, G. Finnveden, Plastic waste as a fuel CO₂-neutral or not? Energy Environ. Sci. 2 (2009) 907.
- [9] U.N.E. Programme, Drowning in Plastics Marine Litter and Plastic Waste Vital Graphics, (2021).
- [10] K. Hu, Y. Yang, Y. Wang, X. Duan, S. Wang, Catalytic carbon and hydrogen cycles in plastics chemistry, Chem Catalysis, (2022).
- [11] C. Wang, H. Han, Y. Wu, D. Astruc, Nanocatalyzed upcycling of the plastic wastes for a circular economy, Coord. Chem. Rev. 458 (2022), 214422.
- [12] M. Chu, Y. Liu, X. Lou, Q. Zhang, J. Chen, Rational design of chemical catalysis for plastic recycling, ACS Catalysis (2022) 4659–4679.

- [13] M. Chu, W. Tu, S. Yang, C. Zhang, Q. Li, Q. Zhang, J. Chen, Sustainable chemical upcycling of waste polyolefins by heterogeneous catalysis, SusMat 2 (2022) 161–185.
- [14] P.A. Kots, B.C. Vance, D.G. Vlachos, Polyolefin plastic waste hydroconversion to fuels, lubricants, and waxes: a comparative study, React. Chem. Eng. 7 (2022) 41–54.
- [15] G. Celik, R.M. Kennedy, R.A. Hackler, M. Ferrandon, A. Tennakoon, S. Patnaik, A. M. LaPointe, S.C. Ammal, A. Heyden, F.A. Perras, M. Pruski, S.L. Scott, K. R. Poeppelmeier, A.D. Sadow, Upcycling single-use polyethylene into high-quality liquid products, Massimiliano Delferro ACS Cent. Sci. 5 (11) (2019) 1795–1803, https://doi.org/10.1021/acscentsci.9b00722.
- [16] I.L. Peczak, R.M. Kennedy, R.A. Hackler, R. Wang, Y. Shin, M. Delferro, K. R. Poeppelmeier, Scalable synthesis of Pt/SrTiO3 hydrogenolysis catalysts in pursuit of manufacturing-relevant waste plastic solutions, ACS Appl. Mater. Interfaces 13 (2021) 58691–58700.
- [17] A. Tennakoon, X. Wu, A.L. Paterson, S. Patnaik, Y. Pei, A.M. Lapointe, S.C. Ammal, R.A. Hackler, A. Heyden, I.I. Slowing, G.W. Coates, M. Delferro, B. Peters, W. Huang, A.D. Sadow, F.A. Perras, Catalytic upcycling of high-density polyethylene via a processive mechanism, Nature, Catalysis 3 (2020) 893–901.
- [18] S.D. Jaydev, A.J. Martín, J. Pérez-Ramírez, Direct conversion of polypropylene into liquid hydrocarbons on carbon-supported platinum catalysts, ChemSusChem 14 (2021) 5179–5185.
- [19] J.E. Rorrer, C. Troyano-Valls, G.T. Beckham, Y. Román-Leshkov, Hydrogenolysis of polypropylene and mixed polyolefin plastic waste over Ru/C to produce liquid alkanes, ACS Sustain. Chem. Eng. 9 (2021) 11661–11666.
- [20] J.E. Rorrer, G.T. Beckham, Y. Román-Leshkov, Conversion of polyolefin waste to liquid alkanes with ru-based catalysts under mild conditions, JACS Au 1 (2020) 8–12.
- [21] C. Wang, T. Xie, P.A. Kots, B.C. Vance, K. Yu, P. Kumar, J. Fu, S. Liu, G. Tsilomelekis, E.A. Stach, W. Zheng, D.G. Vlachos, Polyethylene Hydrogenolysis at Mild Conditions over Ruthenium on Tungstated Zirconia, JACS Au, (2021).
- [22] Y. Nakaji, M. Tamura, S. Miyaoka, S. Kumagai, M. Tanji, Y. Nakagawa, T. Yoshioka, K. Tomishige, Low-temperature catalytic upgrading of waste polyolefinic plastics into liquid fuels and waxes, Appl. Catal. B: Environ. 285 (2021), 119805.
- [23] B.C. Vance, P.A. Kots, C. Wang, Z.R. Hinton, C.M. Quinn, T.H. Epps III, L.T. Korley, D.G. Vlachos, Single pot catalyst strategy to branched products via adhesive isomerization and hydrocracking of polyethylene over platinum tungstated zirconia, Appl. Catal. B: Environ. (2021), 120483.
- [24] C. Jia, S. Xie, W. Zhang, N.N. Intan, J. Sampath, J. Pfaendtner, H. Lin, Deconstruction of high-density polyethylene into liquid hydrocarbon fuels and lubricants by hydrogenolysis over Ru catalyst, Chem Catalysis, (2021).
- [25] W.-T. Lee, F.D. Bobbink, A.P. Van Muyden, K.-H. Lin, C. Corminboeuf, R. R. Zamani, P.J. Dyson, Catalytic hydrocracking of synthetic polymers into gridcompatible gas streams, Cell Reports Physical, Science 2 (2021), 100332.
- [26] S.D.A. Sharuddin, F. Abnisa, W.M.A.W. Daud, M.K. Aroua, A review on pyrolysis of plastic wastes, Energy Convers. Manag. 115 (2016) 308–326.
- [27] X. Wang, T. Jia, L. Pan, Q. Liu, Y. Fang, J.-J. Zou, X. Zhang, Review on the relationship between liquid aerospace fuel composition and their physicochemical properties, Trans. Tianjin Univ. 27 (2021) 87–109.
- Y. Nakaji, D. Kobayashi, Y. Nakagawa, M. Tamura, K. Okumura, K. Tomishige, Mechanism of formation of highly dispersed metallic ruthenium particles on ceria support by heating and reduction, J. Phys. Chem. C. 123 (2019) 20817–20828.
 Y. Nakagawa, Si Oya, D. Kanno, Y. Nakaji, M. Tamura, K.J.C. Tomishige, Reg.
- [29] Y. Nakagawa, Si Oya, D. Kanno, Y. Nakaji, M. Tamura, K.J.C. Tomishige, Reg. React. Mech. Ru-Catalyzed Hydrog. Squalane Model Alkanes 10 (2017) 189–198.
- [30] L. Chen, L.C. Meyer, L. Kovarik, D. Meira, X.I. Pereira-Hernandez, H. Shi, K. Khivantsev, O.Y. Gutiérrez, J. Szanyi, Disordered, Sub-Nanometer Ru Structures on CeO₂ are Highly Efficient and Selective Catalysts in Polymer Upcycling by Hydrogenolysis, ACS Catal. (2022) 4618–4627.
- [31] E. Iglesia, S.L. Soled, R.A. Fiato, Fischer-Tropsch synthesis on cobalt and ruthenium. Metal dispersion and support effects on reaction rate and selectivity, J. Catal. 137 (1992) 212–224.
- [32] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Phys. Rev. B 47 (1993) 558.
- [33] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1996) 15–50.
- [34] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169.
- [35] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys. 132 (2010), 154104.
- [36] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, J. Comput. Chem. 32 (2011) 1456–1465.
- [37] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmentedwave method, Phys. Rev. b 59 (1999) 1758.
- [38] G. Kresse, J. Hafner, Ab initio molecular dynamics for open-shell transition metals, Phys. Rev. B 48 (1993) 13115.
- [39] S. Dudarev, G. Botton, S. Savrasov, C. Humphreys, A. Sutton, Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+ U study, Phys. Rev. B 57 (1998) 1505.
- [40] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, Commentary: the materials project: a materials genome approach to accelerating materials innovation, APL Mater. 1 (2013), 011002.

C. Wang et al.

- [41] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13 (1976) 5188.
- [42] S. Galvagno, G. Capannelli, G. Neri, A. Donato, R. Pietropaolo, Hydrogenation of cinnamaldehyde over Ru/C catalysts: effect of Ru particle size, J. Mol. Catal. 64 (1991) 237–246.
- [43] S. Galvagno, C. Milone, A. Donate, G. Neri, R. Pietropaolo, Influence of metal particle size in the hydrogenation of citral over Ru/C, Catal. Lett. 18 (1993) 349–355.
- [44] B. Coq, P.S. Kumbhar, C. Moreau, P. Moreau, M.G. Warawdekar, Liquid phase hydrogenation of cinnamaldehyde over supported ruthenium catalysts: Influence of particle size, bimetallics and nature of support, J. Mol. Catal. 85 (1993) 215–228.
- [45] Y. Nakaji, Si Oya, H. Watanabe, M.M. Watanabe, Y. Nakagawa, M. Tamura, K.J. C. Tomishige, Prod. Gasol. Fuel Alga-Derived Botryococcene Hydrog. Ceria Ruthenium Catal. 9 (2017) 2701–2708.
- [46] S. Tauster, Strong metal-support interactions, Acc. Chem. Res. 20 (1987) 389–394.[47] G.L. Haller, D.E. Resasco, Metal-support interaction: Group VIII metals and
- reducible oxides. Advances in catalysis, Elsevier., 1989, pp. 173–235.
 [48] B.C. Vance, P.A. Kots, C. Wang, Z.R. Hinton, C.M. Quinn, T.H. Epps, L.T.J. Korley, D.G. Vlachos, Single pot catalyst strategy to branched products via adhesive isomerization and hydrocracking of polyethylene over platinum tungstated zirconia, Appl. Catal. B: Environ. (2021), 120483.
- [49] S. Liu, P.A. Kots, B.C. Vance, A. Danielson, D.G. Vlachos, Plastic waste to fuels by hydrocracking at mild conditions, Sci. Adv. 7 (2021) eabf8283.
- [50] C. Wang, T. Xie, P. Kots, B. Vance, K. Yu, P. Kumar, J. Fu, S. Liu, G. Tsilomelekis, E. Stach, W. Zheng, D. Vlachos, Polyethylene Hydrogenolysis at Mild Conditions Over Ruthenium on Tungstated Zirconia, JACS Au, (Under Review).
- [51] S. Lwin, Y. Li, A.I. Frenkel, I.E. Wachs, Nature of WOx sites on SiO2 and their molecular structure-reactivity/selectivity relationships for propylene metathesis, ACS Catalysis 6 (2016) 3061–3071.
- [52] S. Lwin, I.E. Wachs, Olefin metathesis by supported metal oxide catalysts, ACS Catalysis 4 (2014) 2505–2520.
- [53] Y. Sun, C. Li, I. Djerdj, O. Khalid, P. Cop, J. Sann, T. Weber, S. Werner, K. Turke, Y. Guo, B.M. Smarsly, H. Over, Oxygen storage capacity versus catalytic activity of ceria-zirconia solid solutions in CO and HCl oxidation, Catal. Sci. Technol. 9 (2019) 2163–2172.
- [54] W. Zhou, N. Soultanidis, H. Xu, M.S. Wong, M. Neurock, C.J. Kiely, I.E. Wachs, Nature of catalytically active sites in the supported WO3/ZrO2 solid acid system: a current perspective, ACS Catal. 7 (2017) 2181–2198.
- [55] K. Chen, S. Xie, E. Iglesia, A.T. Bell, Structure and properties of zirconia-supported molybdenum oxide catalysts for oxidative dehydrogenation of propane, J. Catal. 189 (2000) 421–430.
- [56] A. Khodakov, J. Yang, S. Su, E. Iglesia, A.T. Bell, Structure and properties of vanadium oxide-zirconia catalysts for propane oxidative dehydrogenation, J. Catal. 177 (1998) 343–351.
- [57] W. Zhou, E.I. Ross-Medgaarden, W.V. Knowles, M.S. Wong, I.E. Wachs, C.J. Kiely, Identification of active Zr–WO x clusters on a ZrO 2 support for solid acid catalysts, Nat. Chem. 1 (2009) 722.

- Applied Catalysis B: Environmental 319 (2022) 121899
- [58] J. He, S.P. Burt, M. Ball, D. Zhao, I. Hermans, J.A. Dumesic, G.W. Huber, Synthesis of 1,6-Hexanediol from Cellulose Derived Tetrahydrofuran-Dimethanol with Pt-WOx/TiO2 Catalysts, ACS, Catalysis 8 (2018) 1427–1439.
- [59] S. Eibl, R. Jentoft, B. Gates, H. Knözinger, Conversion of n-pentane and of n-butane catalyzed by platinum-containing WO x/TiO 2, Phys. Chem. Chem. Phys. 2 (2000) 2565–2573.
- [60] S. Eibl, B. Gates, H. Knözinger, Structure of WO x/TiO2 catalysts prepared from hydrous titanium oxide hydroxide: influence of preparation parameters, Langmuir 17 (2001) 107–115.
- [61] I.T. Ghampson, G. Pecchi, J.L.G. Fierro, A. Videla, N. Escalona, Catalytic hydrodeoxygenation of anisole over Re-MoO x /TiO 2 and Re-VO x /TiO 2 catalysts, Appl. Catal. B: Environ. 208 (2017) 60–74.
- [62] H.T. Kreissl, M.M.J. Li, Y.-K. Peng, K. Nakagawa, T.J.N. Hooper, J.V. Hanna, A. Shepherd, T.-S. Wu, Y.-L. Soo, S.C.E. Tsang, Structural studies of bulk to nanosize niobium oxides with correlation to their acidity, J. Am. Chem. Soc. 139 (2017) 12670–12680.
- [63] N.H. Hai, N.D. Phu, N.H. Luong, N. Chau, H.D. Chinh, L.H. Hoang, D.L. Leslie-Pelecky, Mechanism for sustainable magnetic nanoparticles under ambient conditions, J. Korean Phys. Soc. 52 (2008) 1327–1331.
- [64] H. Hu, W. Wang, Z. Liu, B. Wang, Z. Li, X. Ma, Sulfur-resistant CO methanation to CH4 over MoS2/ZrO2 catalysts: support size effect on morphology and performance of Mo species, Catal. Lett. 148 (2018) 2585–2595.
- [65] N.D. Evdokimenko, G.I. Kapustin, O.P. Tkachenko, K.B. Kalmykov, A.L. Kustov, Zn Doping Effect on the Performance of Fe-Based Catalysts for the Hydrogenation of CO₂ to Light Hydrocarbons, Molecules 27 (2022) 1065.
- [66] J. Fu, S. Liu, W. Zheng, R. Huang, C. Wang, A. Lawal, K. Alexopoulos, S. Liu, Y. Wang, K. Yu, J.A. Boscoboinik, Y. Liu, X. Liu, A.I. Frenkel, O.A. Abdelrahman, R. J. Gorte, S. Caratzoulas, D.G. Vlachos, Modulating the dynamics of Brønsted acid sites on PtWOx inverse catalyst, Nature, Catalysis 5 (2022) 144–153.
- [67] H.-Y. Lin, Y.-W. Chen, The kinetics of H2 adsorption on supported ruthenium catalysts, Thermochim. Acta 419 (2004) 283–290.
- [68] H. Ishikawa, J.N. Kondo, K. Domen, Hydrogen adsorption on Ru/ZrO2 studied by FT-IR, The, J. Phys. Chem. B 103 (1999) 3229–3234.
- [69] G.C. Bond, J.C. Slaa, Catalytic and structural properties of ruthenium bimetallic catalysts: hydrogenolysis of propane and n-butane on RuAl2O3 catalysts modified by a Group 14 element, J. Mol. Catal. A: Chem. 106 (1996) 135–149.
- [70] D.W. Flaherty, E. Iglesia, Transition-state enthalpy and entropy effects on reactivity and selectivity in hydrogenolysis of n-alkanes, J. Am. Chem. Soc. 135 (2013) 18586–18599.
- [71] G.C. Bond, J.C. Slaa, Analysis of structure-sensitivity in reactions of alkanes: nbutane hydrogenolysis on a Ru/Al 2 O 3 catalyst, Catal. Lett. 23 (1994) 293–298.
- [72] G. Celik, R.M. Kennedy, R.A. Hackler, M. Ferrandon, A. Tennakoon, S. Patnaik, A. M. LaPointe, S.C. Ammal, A. Heyden, F.A. Perras, Upcycling single-use
- polyethylene into high-quality liquid products, ACS Cent. Sci. 5 (2019) 1795–1803.
 [73] M. Salciccioli, Y. Chen, D.G. Vlachos, Microkinetic modeling and reduced rate expressions of ethylene hydrogenation and ethane hydrogenolysis on platinum, Ind. Eng. Chem. Res. 50 (2011) 28–40.
- [74] G.C. Bond, B. Coq, R. Dutartre, J.G. Ruiz, A.D. Hooper, M.G. Proietti, M.C.S. Sierra, J.C. Slaa, Effect of various pretreatments on the structure and properties of ruthenium catalysts, J. Catal. 161 (1996) 480–494.