Rapid atom-efficient polyolefin plastics hydrogenolysis mediated by a well-defined single-site electrophilic/cationic organozirconium catalyst

Synthetic polymers play an essential role in modern society, providing necessary materials for food packaging, infrastructure, transportation, clothing, medical disposables, consumer electronics, etc. In 2018, ca.395 million tons were produced worldwide, with 1.1 billion tons (Gt) projected annually by 2050. Since most plastics are single-use, global production has created a corresponding increase in derived waste and environmental impact. Recycling is an attractive but underutilized means of repurposing plastics, decreasing fossil fuel reliance, and addressing plastics pollution. However, most recycling today is mechanical, with polymers shredded and then re-shaped into materials with inferior properties compared to virgin materials. Polyolefins comprise more than half of the production of modern synthetic polymers due to their low cost, enormous versatility, and chemical inertness. Today polyolefins such as polyethylene, polypropylene, and polystyrene are typically recycled pyrolytically at temperatures >400 °C. However, this energy-intensive unselective cracking yields hydrocarbon mixtures and significant residual carbonaceous coke.

Catalytic polyolefin deconstruction to lighter hydrocarbons has proven challenging due to their chemical/thermal inertness. One homogeneous approach uses an Ir catalyst and metathesis with an alkane to lower the polyolefin molecular mass. The conversion of polyethylene to long-chain alkylaromatics was also demonstrated using a Pt catalyst supported on γ-alumina. Recently, catalytic polyolefin hydrogenolysis has attracted greater attention since it employs...
H₂ as a cost-effective deconstruction agent, and the overall process is thermodynamically favorable. Currently, the most common approaches involve using heterogeneous precious-metal catalysts such as Ru and Pt to transform polyolefins into wax-range and lighter hydrocarbons. Such processes typically employ high temperatures/pressures and extended reaction times16–17.

Regarding earth-abundant metal polyolefin hydrogenolysis catalysts, the only example to our knowledge employed a formally neutrally charged d⁰ Zr alkyl bound to silica-alumina, which mediates slowly hydrogenolysis (Fig. 1a). This formally neutral charged Zr alkyl was reported by Basset et al. to have ca. 3% of the activity now found for the catalyst reported here (vide infra)18. We hypothesized that the protonolytic chemisorption of Zr alkyls on very different, highly Bronsted acidic surfaces would create weak/weakly coordinatively bound formal cationic organozirconium adsorbates on such Bronsted acidic oxides yields methane via Zr–CH₃ bond protonolysis and an electrostatically bound, formally cationic organozirconium adsorbate (Fig. 1b). This surface-bound formally cationic species catalyzes very rapidly,facially selective arene hydrogenation and olefin polymerization with nearly 100% of the Zr sites catalytically significant19,20. Such catalysts operate via mechanisms differing substantially from later transition metal catalysts, raising the intriguing question of whether they might rapidly activate/hydrogenolyze polyolefins via well-defined but unconventional pathways.

Here we report that ZrNp₄ chemisorption on sulfated alumina (Hammatt acidity, H₀ ≈ −14.6)21 yields AlS/ZrNp₂, characterized by solid-state nuclear magnetic resonance (NMR) spectroscopy and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and density-functional theory (DFT) computation (Fig. 1c, d). We report that AlS/ZrNp₂ catalyzes the rapid, solventless hydrogenolysis of polyethylene (PE), isotactic polypropylene (i-PP), polyethylene-co-1-octene (PECO) copolymer, and consumer PE under very mild conditions25. For polyethylene, hydrogenolysis to light hydrocarbons proceeds with activity as high as 4000 mol(CH₂ units) mol(Zr)⁻¹ h⁻¹ at 200°C under 2.0 atm H₂ (Fig. 2, Eq. (1)). Remarkably, <48 min, the starting PE is entirely consumed and converted into liquid and volatile products. To our knowledge, this is the most rapid catalytic PE hydrogenolysis process reported to date in the open literature and is surprising considering the low catalyst loading, mild reaction conditions, and simple reactor setup (high-pressure glass flask + magnetic stirring bar). The reaction is extremely fast, with a calculated activity of ~4000 mol(CH₂ units) mol(Zr)⁻¹ h⁻¹ (Table 1, Entry 1).

Polyolefin hydrogenolysis products were analyzed as follows. At the end of the reaction, the reactor is cooled to 25°C in a water bath, and the reactor headspace contents analyzed by GC/FID. Next, the remaining volatiles are vented, the residual liquid + higher molecular mass solid saturated hydrocarbon products are stirred with DCM, and the resulting suspension is filtered. The reactor components are then rinsed several times with DCM to ensure the collection of all solid and DCM-soluble liquid products. The filtrate is collected, the DCM is evaporated under ~1 Torr reduced pressure, and the resulting hydrocarbons are weighed. The mass of this product gives the yield of the DCM extract fraction, which is analyzed by GC/MS (gas chromatography/mass spectrometry). We find that the DCM extraction and evaporation under reduced pressure results in <5 wt% loss of the volatile liquid hydrocarbons. After isolation via filtration, the DCM-insoluble higher molecular mass saturated hydrocarbon fraction is collected, dried, and weighed. The mass of this fraction, corrected for the weight of the catalyst, gives the yield of the solids fraction. The solid product contents are then analyzed by gel permeation chromatography (GPC). The volatiles fraction mass is the mass not accounted for after measuring the solids and DCM extract fractions, and its composition is readily analyzed via headspace gas chromatography/flame ionization detection (GC/FID). The combined mass of the volatiles and DCM extract fractions as a percentage of the initial reactant polyolefin mass is taken as the percent conversion for a given polyolefin hydrogenolysis reaction. These analytical methods for handling polyolefin hydrogenolysis products

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**Fig. 1**: Schematic depiction of zirconium alkyl surface chemistry on various oxide surfaces. a. Zr alkyl-derived adsorbate on a relatively weak Bronsted acidic surface, providing relatively strong conjugate Bronsted base counteranions. b. CpZr(CH₃)₃-derived adsorbate on a very strong Bronsted acidic surface (AlS = sulfated alumina). c. ZrNp₄-derived (Np = neopentyl) adsorbate on a very strong Bronsted acidic surface followed by H₂ exposure. d. ZrNp₄ protonolytic chemisorption on strongly Bronsted acidic sulfated alumina (AlS), and generation of the corresponding electrophilic hydride via Zr–Np α-bond metathesis, which is common in d⁰ metal catalysis26,27, in accord with the DFT computation.

**Results**

**Catalytic polyolefin hydrogenolysis**

Linear polyethylene (PE) homopolymer, isotactic polypropylene (i-PP), polyethylene-co-1-octene (PECO), and a post-consumer high-density polyethylene (HDPE) blue-dyed food container cap were initially investigated. Thus, 1.5 g of PE was heated with AlS/ZrNp₂ (0.03 mol%) at 200°C under 2.0 atm H₂ (Fig. 2, Eq. (1)). Interestingly, in <48 min, the starting PE is entirely consumed and converted into liquid and volatile products. To our knowledge, this is the most rapid catalytic PE hydrogenolysis process reported to date in the open literature and is surprising considering the low catalyst loading, mild reaction conditions, and simple reactor setup (high-pressure glass flask + magnetic stirring bar). The reaction is extremely fast, with a calculated activity of ~4000 mol(CH₂ units) mol(Zr)⁻¹ h⁻¹ (Table 1, Entry 1).

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are similar to those used in the recent polyolefin hydrogenolysis literature.\textsuperscript{32,34,28}

To analyze the reaction products in more detail, the reaction was slowed by decreasing the temperature to 150 °C and monitored at varied time intervals, with reactions halted periodically by cooling to 25 °C (Eq. (1)). The time dependence of PE hydrogenolysis with varied time intervals, with reactions halted periodically by cooling to 150 °C and monitored at 200 °C >99% after 48 min 150 °C >95% after 2h.

![Diagram](PE_Hydrogenolysis)

**Fig. 2 | Catalytic hydrogenolysis of linear polyethylene (PE).** a Temporal product distributions for AlS/ZrNp\textsubscript{2}-catalyzed PE hydrogenolysis (150 °C, 2.0 atm H\textsubscript{2}, 0.03 mol% Zr). b Headspace volatiles GC/FID chromatogram for 30 min PE hydrogenolysis. c GC/MS chromatograms of DCM extracts from AlS/ZrNp\textsubscript{2}-catalyzed PE hydrogenolysis. Trace chain branching is denoted by ▼. d Gel permeation chromatograms (GPC) of solid fractions from the same PE hydrogenolysis experiments. Number-average alkane product chain lengths are shown above the respective traces. The GPC calibration range is denoted by black lines.

While linear PE homopolymers are an informative substrate due to their relatively low melting points and simple structures, i-PP and PECO are of greater technological significance.\textsuperscript{29} The AlS/ZrNp\textsubscript{2} catalyst was next applied to these materials at 190 °C to lower the melt viscosity for ease of stirring (Fig. 3, Eq. (2)). Reacting 1.0 g i-PP (M<sub>n</sub> = 36 kgmol\textsuperscript{-1}) over 0.04 mol% AlS/ZrNp\textsubscript{2} under 2 atm H\textsubscript{2} effects quantitative conversion to 68% low-molecular-weight (M<sub>n</sub> < C30) products and 28% C1–C6 volatiles in only 1 h (Table 1, entry 5, Fig. 3a, b). The i-PP DCM extract GC/MS chromatogram has greater complexity than that of PE since the product alkanes are not only linear and have significant ethyl- and methyl-branching, reflecting the different PP chain cleavage points (Fig. 3c). The DCM extract number average molecular mass (M<sub>\text{DCE}</sub>) also falls with increasing conversion, and the distribution narrows as for PE (Fig. 3c). Stirring PECO (M<sub>n</sub> = 7.0 kgmol\textsuperscript{-1}, 2.5% 1-octene incorporation) reaction mixtures was challenged by the substantial melt viscosity. Nevertheless, hydrogenolysis proceeds rapidly to afford 85% volatile and DCM-soluble (M<sub>n</sub> < C18) products and 28% C1–C6 volatiles in only 1 h (Fig. 3a, b). The i-PP DCM extract GC/MS data are similar, probably reflecting H\textsubscript{2} starvation and yielding a most probable chain length of ~15 carbons (Fig. 3d). Low-molecular weight alkane branching (~1%) is present, probably from the enchained 1-octene comonomer. Comparative hydrogenolysis rates with post-consumer HDPE (M<sub>n</sub> = 9.9 kgmol\textsuperscript{-1}) are achieved at 200 °C/2.0 atm H\textsubscript{2}/alumina proceeds at ~3% of the rate of the present reactions catalyzed by AlS/ZrNp\textsubscript{2} (Table 1, Entry 4).
### Table 1 | Polyolefin and n-Hexadecane (C16) hydrogenolysis data over AlS/ZrNp2

| Entry | Substrate | Temperature (°C) | H₂ pressure (atm) | Reaction time (min) | Catalyst loading (Zr mol%) | Substrate conversion (%) | Activity (h⁻¹) |
|-------|-----------|------------------|-------------------|---------------------|----------------------------|--------------------------|-----------------|
| 1     | PE        | 200              | 2.0               | 48                  | 0.03                       | >99(1)                   | 4014(54)       |
| 2     | PE        | 150              | 2.0               | 30                  | 0.03                       | 32(1)                    | 2088(28)       |
| 3     | PE        | 150              | 2.0               | 120                 | 0.03                       | 95(1)                    | 1566(22)       |
| 4     | PE        | 150              | 1.0               | 120                 | 0.29                       | 25(1)                    | 43             |
| 5     | i-PP      | 190              | 2.0               | 60                  | 0.04                       | 96(2)                    | 2193(40)       |
| 6     | PECO      | 190              | 2.0               | 60                  | 0.04                       | >99(2)                   | 2995(52)       |
| 7     | HDPE food container cap | 200 | 2.0 | 80 | 0.02 | 45(2) | 1520(29) |
| 8     | C16       | 150              | 2.0               | 18                  | 0.05                       | >99                      | 690            |
| 9     | C16       | 90               | 2.0               | 90                  | 0.02                       | 15(1)                    | 56(7)          |
| 10    | C16       | 150              | 2.0               | 1440                | 0.00                      | Trace                    | Trace          |
| 11    | C16       | 150              | 2.0               | 30                  | 0.01                       | Trace                    | Trace          |
| 12    | C16       | 120              | 0.5               | 15                  | 0.02                       | 12(1)                    | 26(20)         |
| 13    | C16       | 120              | 4.0               | 15                  | 0.02                       | 12(1)                    | 26(20)         |

*Reaction in 350 mL heavy-walled glass pressure vessels.

*Catalyst loading with respect to CH₂ units for all substrates. All saturated polyolefins are principally comprised of CH₂ units, thus all polyolefin hydrogenolysis activities and catalyst loadings are reported with respect to CH₂ units.

Polyolefin hydrogenolysis activity: mol(CH₂ units of CH₂Cl₂-soluble hydrocarbons + volatiles) mol(Zr)⁻¹ h⁻¹; C16 activity: mol(C16) mol(Zr)⁻¹ h⁻¹.

Uncertainty in activity estimated from analytical uncertainty in percent conversion.

Polyolefin conversion = yield of combined volatiles + CH₂Cl₂-soluble hydrocarbons; uncertainty in polymer hydrogenolysis activity and conversion reflects an estimated maximum of 20 mg solids loss during reaction workup; see SI for details regarding the estimation of uncertainties.

Conversion was defined as the amount of C1–C9 hydrocarbons produced as a percentage of initial polymer mass.

Control experiment without Zr.

Hydrogenolysis reaction catalyzed by Cp*Zr(CH₃)₃ supported on AlS₃8.

Trace C13–C15 hydrocarbons not attributable to starting C16 detected in GC-MS.

Uncertainty in activity and conversion is ±3 standard deviations of all activities in varied pressure experiments.

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**Fig. 3** | Catalytic hydrogenolysis of branched polyolefins. **a** Temporal product distributions for the AlS/ZrNp₂-catalyzed i-PP hydrogenolysis (190 °C, 2.0 atm H₂, 0.04 mol% Zr). **b** GC/MS chromatograms of DCM extracts from i-PP experiments. **c** Temporal product distributions for AlS/ZrNp₂-catalyzed PECO hydrogenolysis (190 °C, 2.0 atm H₂, 0.04 mol% Zr). **d** GC/MS chromatograms of DCM extracts from PECO experiments.
0.02 mol% Zr loading in 80 min (Table 1, Entry 7). Furthermore, note that the deliberate introduction of ~5 mL of ambient air (1:1 O₂:Zr ratio) into the reaction headspace prior to beginning the reaction has no measurable effect on catalyst activity (SI p. S5).

**Kinetic studies with a model saturated hydrocarbon**

Liquid n-hexadecane (C16; b.p. = 287 °C) served as a realistic PE reactivity/rheology model. The C16 conversion is defined as the mass of C16 consumed over the course of a given reaction. This is quantified via GC/MS. For polyolefins, it is defined as the mass of volatile and DCM-soluble hydrocarbons produced. Measurements as a function of stirring rate showed that stirring at ≥600 RPM minimizes mass transport effects (Fig. S8). For example, 1.93 mL of C16 over AlS/ZrNp2 (0.05 mol% Zr) at 150 °C/2.5 atm H₂ (350 mL vessel) is completely converted to C1–C15 hydrocarbons in as little as 18 min as assessed by GC/MS and GC/FID (Eq. (3), Table 1, Entry 8; Video S1). Similar to the PE hydrogenolyses, the products are linear even and odd carbon number hydrocarbons, with ~1% methyl branched alkanes (Figs. S12–S14). Interestingly, the AlS/ZrNp2-catalyzed hydrogenolysis of C16 begins at temperatures as low as 90 °C (Table 1, Entry 9). A 24 h control with only C16 + AlS + H₂ yields negligible hydrogenolysis products (Table 1, entry 10, Fig. S9). The above results argue that C16 is a valid PE model. Hydrogenolysis of C16 begins at temperatures as low as 90 °C (Fig. 5a, b) with a characteristic 8.11 ppm 'H Zr–H NMR signal (~3), not present in D2 reactions (Fig. S4). The rapidity of this hydrogenolysis was also verified by gas-phase 'H NMR monitoring of the AlS/ZrNp2 + H₂ reaction (SI p. S16 and Fig. S11). Besides weakened C–H alkyl signals, resonances at 82.0 and 87.5 ppm are also visible and tentatively assigned to Al–OH and Al–H groups, respectively (~2.26 Å average) and two Zr–O bonds in excellent agreement with the EXAFS data (Table 2, entry 1). DrFTIR vibrational spectra reveal νZr–H and νAl–H stretching modes at 1620 and 1930 cm⁻¹, respectively (Fig. 5c), not present in AlS/ZrNp2 (Fig. 5c). Furthermore, exposing AlS/ZrNp2 to D₂ significantly weakens these features, supporting the νZr–H and νAl–H assignments (Fig. S5). Additionally, the AlS/ZrNp2 3000–2800 cm⁻¹ alkyl νC–H modes diminish in intensity upon H₂ exposure, supporting Zr-neopentyl → AlS/ZrH(Np) conversion (Fig. 5c). Interestingly, on exposing AlS/ZrH(Np) to pentane vapor, the Zr–H ν11 ppm ppm NMR signal and the 1620 cm⁻¹ vibration vanish, however, the signals at 87.5 ppm and 1930 cm⁻¹ remain (Fig. S6), arguing the latter represent less reactive Al–H species.

**Catalyst structural and reaction mechanism characterization**

Using the aforementioned procedures, AlS/ZrNp2 with a Zr loading of 1.40 wt% (~0.2 Zr/nm²) was prepared by rigorously anaerobic Zr(neopentyl)₂ chemisorption on AlS (Fig. 5a). Solid-state 'H magic angle spinning (MAS) NMR spectroscopy reveals a 6.09 ppm signal assignable to Zr–Np CH₃ and CH₂ moieties (Fig. 5b). Interestingly, upon H₂ exposure at 150 °C/30 min, one or more neopentyl ligands are hydrogenolyzed, yielding HNp and a proposed Zr–H species, AlS/ZrH(Np) (Fig. 5a, b) with a characteristic 8.11 ppm 'H Zr–H NMR signal (~3), not present in D₂ reactions (Fig. S4). The rapidity of this hydrogenolysis was also verified by gas-phase 'H NMR monitoring of the AlS/ZrNp2 + H₂ reaction (SI p. S16 and Fig. S11). Besides weakened C–H alkyl signals, resonances at 82.0 and 87.5 ppm are also visible and tentatively assigned to Al–OH and Al–H groups, respectively (~2.26 Å average) and two Zr–O bonds in excellent agreement with the EXAFS data (Table 2, entry 1). DrFTIR vibrational spectra reveal νZr–H and νAl–H stretching modes at 1620 and 1930 cm⁻¹, respectively (Fig. 5c), not present in AlS/ZrNp2 (Fig. 5c). Furthermore, exposing AlS/ZrNp2 to D₂ significantly weakens these features, supporting the νZr–H and νAl–H assignments (Fig. S5). Additionally, the AlS/ZrNp2 3000–2800 cm⁻¹ alkyl νC–H modes diminish in intensity upon H₂ exposure, supporting Zr-neopentyl → AlS/ZrH(Np) conversion (Fig. 5c). Interestingly, on exposing AlS/ZrH(Np) to pentane vapor, the Zr–H ν11 ppm ppm NMR signal and the 1620 cm⁻¹ vibration vanish, however, the signals at 87.5 ppm and 1930 cm⁻¹ remain (Fig. S6), arguing the latter represent less reactive Al–H species.

**Zr EXAFS and DFT computation provide additional chemical and electronic structural information.** The former indicates that AlS/ZrNp2 is an oxide-bound ZrNp₂ species having three rather long Zr–O bonds (~2.26 Å average) and two Zr–C bonds (Fig. 5d, e; Table 2, entry 1). The DFT-derived model for AlS/ZrNp2 (Fig. 5d) reveals three 2.18–2.24 Å Zr–O bonds in excellent agreement with the EXAFS data (Table 2, entry 1). Operando EXAFS monitoring of AlS/ZrNp2 hydrogenolysis reveals gradual conversion to AlS/ZrH(Np), with the Zr–C bond number falling from 2.0 (AlS/ZrNp2) to 1.0 (AlS/ZrH(Np)) and a slight average Zr–O bond length contraction to ~2.19 Å (Fig. 5d, e; Table 1, entry 2), consistent with the less encumbered hydride ligand replacing Np. Further H₂ treatment at 150 °C affects minimal change, demonstrating that AlS/ZrH(Np) is stable under catalytic conditions. From the DFT analysis, the three AlS/ZrH(Np) Zr–O bonds are slightly contracted to 2.10–2.20 Å, in accordance with the EXAFS data. Additionally, the DFT-computed 1704 cm⁻¹ AlS/ZrH(Np) νZr–H frequency compares favorably with the 1620 cm⁻¹ DRFTIR value, further supporting the structure in Fig. 5d (Table 2, entry 2). AlS/ZrH(Np) pentane exposure affords an AlS/Zr(alkyl)₂ species having three Zr–O bonds and two Zr–C bonds (Fig. 5d, see SI), in agreement with the NMR and DRFTIR data (Fig. S6). Note that the AlS/ZrNp₂ and AlS/ZrH(Np) Zr–O bonds are significantly
elongated vs. those in neutrally charged 2,6- tBu2PhOZr(benzyl)3 (Zr–O=1.94Å) and (L(Me)AlO)2Zr(benzyl)2 (L = (2,6-iPr2C6H3NC(Me))2CH) (Zr–O=1.91Å; Fig. 5d, Table 2, entries 3, 4)36, and for formally neutrally charged SiO2/Zr–H(1.95 Å; Table 2, entry 5)37, with shorter Zr–O bonds suggesting more covalent σ-bonding, and longer Zr–O bonds greater electrostatic character between the electron-deficient Zr centers and weakly basic AlS oxide ligands23,38,39. Also, the XANES Zr K-edge energies for AlS/ZrNp2 (18.005 keV), AlS/ZrH(Np) (18.008 keV), and AlS/Zr(alkyl)2 (18.006 keV) lie in the range of cationic complexes vs. neutrally charged Bu3PhOZr(benzyl)3 (17.998 keV) and Zr(benzyl)4 (17.999 keV) (Fig. 5f)22. Finally, AlS/ZrH(Np) charge partition analysis computation40 reveals that the Zr atom in model (EtO)2Zr(neopentyl)2 bears a +1.66 charge vs. +1.99 in AlS/ZrH(Np). Calculated Zr–O distances are, (EtO)2Zr(neopentyl)2, 1.93 Å, and AlS/ZrH(Np), 2.10–2.20 Å.

Discussion
Reaction mechanism

Early transition metal d0 reaction pathways differ distinctly from those of most later metal systems and frequently involve combinations of
four-center \(\pi\)-bond metathesis and/or \(C=\pi\times\pi\) insertion/extrusion. For the challenging cleavage of polyolefin C–C bonds, as mediated by the present very unusual surface catalysts, two turnover-limiting scenarios were examined: (1) \(\pi\)-bond metathesis\(^{4,11}\) and (2) \(\beta\)-alkyl transfer\(^{26,27}\). From the present empirical rate law, \(v = k([\text{Zr}]^{1}[\text{H}_{2}]^{0}[\text{C}_{16}]^{0})\), with [C16] in large excess, we infer that the turnover-limiting step or any preceding steps in rapid equilibrium do not involve direct \(\text{H}_{2}\) attack at the catalytic center. From the adsorbate structures, kinetic data, control experiments, and literature precedent, DFT reaction coordinates were computed for scenarios (1) and (2) using \(n\)-dodecane as a model, in Fig. 6a, b, respectively\(^{16,19,20}\). As for catalyst choice, note that a multitude of AlS/ZrH(R) species (R = alkyl or H) of similar energies are doubtless rapidly equilibrating via \(C\–H\ \pi\)-bond metathesis processes (Fig. 6c). AlS/ZrH was selected for simplicity; however, similar pathways are conceivable for other AlS/ZrH(R) species. For \(C\–C\) scission via \(\pi\)-bond metathesis (Fig. 6a), this pathway has a remarkably prohibitive \(76\) kcal/mol computed barrier. Indeed, an experiment with a 1:1 ratio of ethane and \(\text{H}_{2}\) (1 atm total pressure) over a relatively high AlS/ZrH(Np) loading (0.9% mol Zr) reveals negligible hydrogenolysis at \(150^\circ\text{C}\) for 1 h (Eq. 4).

\[
\text{H}_2\text{C} \cdots \text{H}_3\text{C} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2 \quad (4)
\]

| Entry | Species | Bond | Experimental bond length (Å) | DFT bond length (Å) | Alkyl C–H | Alkyl C–H |
|-------|---------|------|-----------------------------|-------------------|------------|------------|
| 1     | AlS/ZrNp₂ | Zr–O1 | 2.26(2)⁴ | 2.24 | 2.958 | 3041 |
|       |         | Zr–O2 | 2.26(2)⁴ | 2.20 | 2.958 | 3041 |
|       |         | Zr–O3 | 2.26(2)⁴ | 2.18 | 2.868 | 2679 |
|       |         | Zr–C1 | 2.42(3)⁵ | 2.12 | 2.42(3)⁵ | 2.22 |
|       |         | Zr–C2 | 2.42(3)⁵ | 2.12 | 2.42(3)⁵ | 2.22 |
| 2     | AlS/ZrH(Np) | Zr–O1 | 2.29(3)⁴ | 2.20 | 2.963 | 3040 |
|       |         | Zr–O2 | 2.14(3)⁴ | 2.10 | 2.963 | 3040 |
|       |         | Zr–O3 | 2.14(3)⁴ | 2.15 | 2.870 | 2966 |
|       |         | Zr–C | 2.38(3)⁴ | 2.20 | 2.963 | 3040 |
|       |         | Zr–H | N.D. | 1.83 | 1620 | 1704 |
| 3     | 2,6-Bu₂PhOZrBn₃ | Zr–O1 | 1.94(1)⁶ | 2.279(2)⁴ | 1.95(3) | N.D. |
|       |         | Zr–O2 | 1.94(1)⁥ | 1.95(3) | N.D. | N.D. |
|       |         | Zr–C | 2.26(3)⁴ | 2.26(3)⁴ | N.D. | N.D. |
| 4⁴ | (LMeAlO)₂ZrBn₂ | Zr–O1 | 1.913(14)⁴ | 1.914(14)⁴ | N.D. | N.D. |
|       |         | Zr–O2 | 1.913(14)⁴ | 1.914(14)⁴ | N.D. | N.D. |
|       |         | Zr–C | 2.265(2)⁴ | 2.265(2)⁴ | N.D. | N.D. |
|       |         | Zr–C | 2.289(2)⁴ | 2.289(2)⁴ | N.D. | N.D. |
| 5⁴ | SiO₂/ZrH | Zr–O1 | 1.94 (1)⁴ | 2.14 | 1.638 | Zr–H N.A. |

\(^{1}\) Bond lengths from EXAFS.
\(^{2}\) Bond lengths from single-crystal X-ray diffraction.
\(^{3}\) Average of 3 bond lengths.
\(^{4}\) Reference 35.
\(^{5}\) Reference 37.

In conclusion, an earth-abundant single-site formally cationic \(\text{Zr}\)-alkyl/hydride catalyst was synthesized on highly Brønsted acidic sulfated alumina and characterized by solid-state \(^1\)H MAS and \(^{13}\)C CPMAS-NMR, DRIFTS, ICP/AES, XANES, EXAFS, DFT, and evaluated for polyolefin and hexadecane (C16) hydrogenolysis. This catalyst mediates very rapidly (690 mol \(\text{C}_{16}\) mol Zr\(^{−1}\) h\(^{−1}\)) hexadecane hydrogenolysis under relatively mild conditions (18 min, \(150^\circ\text{C}\), 2.5 atm \(\text{H}_{2}\)). Under similar solventless conditions, polyethylene, polyethylene-co-1-ctcne, isostatic polypropylene, and commercial post-
consumer polyethylene are rapidly hydrogenolysed to low molecular mass hydrocarbons under mild conditions (150–200 °C/2 atm H2) at low catalyst loadings (0.02–0.04 mol% Zr). Experimental results combined with DFT computation reveal that the turnover-limiting step in alkane/polyolefin C–C scission/chain shortening is intramolecular β-alkyl transfer, in contrast to the σ-bond metathesis process common in much early transition metal catalytic chemistry. The catalytic species, a supported electrophilic Zr-hydride, is readily formed during the hydrogenolysis process. These results convey implications for deconstructing other polymers and inventing new catalysts to achieve this.

Methods

All procedures for air- and moisture-sensitive compounds were carried out with rigorous exclusion of O2 and moisture in flame- or oven-dried Schlenk-type glassware interfaced to a high-vaccum (10⁻⁵–10⁻¹ Torr) line or in an argon-filled M-Braun glovebox with a high capacity recirculator (<1 ppm O2). Argon used on high-vacuum lines (Airgas, UHP-grade) was purified by passage through an oxygen/moisture trap (Matheson, model MTRP-0042-XX). Zirconium(IV) chloride and neopentylmagnesium chloride (1.0 M solution in Et2O) were purchased from Sigma and used without further purification. Tetrakis(neopentyl)zirconium (ZrNp4) was synthesized according to a modification of a literature procedure. In a typical synthesis, neopentylmagnesium chloride (4.4 mmol) was added dropwise to a suspension of ZrCl4 (1.0 mmol) in ether at −78 °C. The mixture was allowed to stir for 2 h, slowly warmed to room temperature, then stirred for an additional 2 h at room temperature. The solvent was removed in vacuo, and the resulting solids were extracted with pentane. The pentane filtrate was isolated, and the solvent was removed in vacuo to yield a colorless solid. The crude product was purified by sublimation at 70 °C and -10⁻¹ Torr, yielding a colorless microcrystalline solid with 83% yield. Polymers were dried in the melt (130–165 °C) under a high vacuum for 48 h before use in the hydrogenolysis reactions.

Physical and analytical measurements

Inductively coupled plasma (ICP) analysis was performed by Gallbraith Laboratories Inc., Knoxville, TN, USA. ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra of hydrogenolysis products were obtained with a Bruker Avance III system equipped with a DB5 column (oven program: 1. 2 min. 50 °C hold 2. 30 °C/min ramp 3. 2 min hold at 300 °C). Split mode injection at 2 μL/injection and a 100:1 split ratio was used. For GC–MS quantification of n-hexadecane, a four-point calibration (0.1, 0.2, 0.3, 0.4 μg/mL) was carried out for each group of samples analyzed by GC/MS with a target sample concentration of 0.2 μg/mL. Calibration standards were prepared in 1,1,2,2-tetrachloroethane (TCE) and stored in airtight Teflon-valved...
glassware. Diffuse reflectance infrared spectroscopy (DRIFTS) measurements were taken under Ar on Thermo 6700 infrared spectrometer equipped with a Harrick Praying Mantis DRIFTS attachment. ZnS windows were used for the DRIFTS cell. Anhydrous KBr with an Ar glovebox atmosphere in the cell was used as a background. BET surface area measurements were carried out with a Micromeritics 3Flex Surface Characterization Analyzer.

X-ray absorption spectroscopy
X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements at Zr K-edge (17,998 eV) were performed at the 5 BM-D beamline of the DND-CAT at the Advanced Photon Source. A double Si (111) monochromator was used for energy selection with an energy resolution of ΔE/E = 1.4 × 10−3. The X-ray energy was calibrated using a metallic Zr foil. The incident X-ray intensity was measured by a spectrometry-grade ionization chamber (MFB-Oxford) filled with 600 He/100 eV (Torr) and was detuned to 60% of its maximum for harmonic rejection. EXAFS spectra were collected in fluorescence mode using a passivated implanted planar silicon (PIPS) detector (Canberra). The sample and the detector were positioned 45° and 90°, respectively, to the X-ray beam direction. Energy scans were executed from 250 eV below to 550 eV above the Zr K edge, which produces the EXAFS spectrum. The catalyst AIS/ZrNp2 with a Zr loading of 1.40 wt% was pressed into a sample holder for the EXAFS measurements. The samples were sealed airtight in a THMS600 Linkam cell inside the glove box, which was pressured with ultrapure Ar gas. Positive Ar pressure was maintained throughout the measurement. After measuring the AIS/ZrNp2 sample, in-situ catalyst hydrogenolysis was carried out by flowing H2 gas with a flow rate of 50 sccm at room temperature with EXAFS data collected every 15 min for 2 h until no further changes were observed. This was followed by heating the sample to 150 °C with continued H2 flow. Data were collected every 15 min for up to 2 h. No changes were observed after this step of the treatment. There was a change in the structure during the hydrogenolysis reaction at room temperature, and these data are shown in the manuscript (Fig. 5e). XANES data extraction, normalisation, and background subtraction was performed using Demeter:Athena. EXAFS data analysis was carried out using the software Demeter-Artemis. The bond lengths (R) and coordination number (N) were obtained by a least-square fit in the R-space of the nearest neighbors using k2-weighted Fourier transform fitting parameter. For data analyses, a standard reference model compound was used: powder 2,6–Bu2PhOZrBn3, which was measured in fluorescence mode.

Computational details
DFT-based simulations were performed with the/Quickstep package, using a hybrid Gaussian and plane wave method44. A double-quality DZVP Gaussian basis set was employed for the Al and Zr atoms, and a triple-quality TZVP Gaussian basis set was employed for all the other atoms45. The Goedecker–Teter–Hutter pseudopotentials46 together with a 400 Ry plane wave cutoff were used to expand the densities obtained with the Perdew–Burke–Ernzerhof (PBE)47 exchange-correlation density functional, and vdW forces are taken in account with the Grimme D3 Method48. Only the gamma point was considered in a supercell approach. Periodic boundary conditions are applied in all directions of space. Molecular graphics were produced by the CHEMCRAFT graphical package49. Enthalpic and entropic contributions along the reaction pathway were evaluated by performing the frequency calculation of the molecular species at 298.15 K and 1 atm as implemented in the G16 code50. In this context, adsorbed catalysts were modeled by simple molecular species, and only the entropic contribution related to vibrational motion is considered. G16 calculations were performed at the level of the B3LYP hybrid functional. The standard all-electron 6–311G* basis set was used for all atoms. The enthalpic and entropic contributions were then “appended” to the SCF energy profile to obtain the Gibbs free energy profile.

General hexadecane hydrogenolysis procedure
In the glovebox, C16 (typically 0.50 g) was passed through a 0.22-μm PTFE syringe filter directly into a dry heavy-walled glass pressure reactor (350 mL volume) containing a 10 mm ovoid stir bar. The desired amount of AIS/ZrNp2 (typically 25 mg, 0.02 mol% Zr) was added to the reactor and was sealed with a threaded Teflon cap with an NPT valve installed. The vessel was carefully removed from the glovebox and interfaced with a high-pressure/high-vacuum line. The reactor was degassed at room temperature (30 s), then charged to the desired pressure of H2. The reactor was placed in an oil bath set to the desired reaction temperature. Once the oil bath thermocouple reached reaction temperature, the time interval was started. At the end of the time interval, the reactor was removed from the oil bath, then cooled via a water bath to room temperature. Headspace samples were taken, if needed, at this point. Note, for determining reaction conversion as a function of time, the reaction temperature was decreased to 90 °C to keep reaction conversions below 15% and preserve the accuracy of the apparent reaction rate. The reactor was vented through the NPT valve and opened to air. Approx. 5 mL of dichloromethane (DCM) or TCE was used to wash the Teflon cap and the interior of the NPT valve. The washings were transferred to a syringe equipped with a 0.22 μm PTFE filter. The reactor was washed 4× with ~10 mL portions of clean solvent, with each washing being added to the syringe. The washings were passed through the filter directly into a 100 mL volumetric flask. The filter was washed 4× with ~5 mL portions of clean solvent, with washings being added to the volumetric flask. Pipettes used to transfer solvent solutions were also washed with clean solvent and added to the volumetric flask. The solution was diluted to the calibration mark, then diluted further using standard analytical techniques to ~0.2 mg/mL. A four-point external calibration (0.1, 0.2, 0.3, and 0.4 mg/mL) of hexadecane in TCE was used to determine the concentration of the sample via GC/MS. The series of external calibration standards were run for each round of reaction sample measurements. Uncertainty in kinetic measurements was taken to be ±1% (absolute) to account for analytical uncertainty, except in the case of varied H2 pressure experiments, where uncertainty was taken to be 3 standard deviations of the data set.

General polyolefin hydrogenolysis procedure
In the glovebox, AIS/ZrNp2, and the desired amount of polymer were loaded into a dry heavy-walled glass pressure reactor (350 mL volume) containing a 10 mm ovoid stir bar, typically with ~15% mass loading of catalyst (0.02–0.04 mol% Zr). The easily implemented and versatile hydrogenolysis reactor and analytical procedures serve four functions: (i) for constant polymer and catalyst, to screen products as a function of reaction conditions such as temperature, H2 pressure, reaction time, and stirring rate. (ii) For constant polymer and reaction conditions, to screen different catalysts in terms of relative activity and product mix selectivity. (iii) For constant catalyst and reaction conditions, to screen different polymers in terms of relative activity and product mix selectivity. (iv) The optically transparent heavy-wall glass reactor can be filled in the glove box, is high-vacuum line compatible, and allows ready visualization of the reaction progress (solid → liquid → gas) as well as stirrer malfunction or possible coking formation (never observed). The polymers were prepared by shaving from a larger puck of pre-melted stock. The reactor was sealed with a threaded Teflon cap having an installed NPT valve. The vessel was carefully removed from the glovebox and interfaced with a high-pressure/high-vacuum line. The reactor was degassed at room temperature (30 s), then charged to 2 atm H2. The reactor was then placed in an oil bath set to the desired temperature (polyethylene 150 °C, polypropylene, polyethylene-co-1-octene, HDPE food container cap 190 or 200 °C). Once the polyolefin melted and contacted the catalyst in the melt, the time interval was
started. Stirring was typically set to 300 rpm initially, then increased to ~800 rpm after a sufficient decrease in polymer viscosity. At the end of the time interval, the reactor was removed from the oil bath, then air-cooled to room temperature. Headspace samples were taken at this point. Headspace samples were collected by the expansion of the reactor contents into an evacuated 500 mL Teflon-valved glass bulb. Individual samples for analysis were taken via septum and gas tight headspace syringe (1 mL). The reactor was vented through the NPT valve and opened to air. Approx. 5 mL DCM was used to wash the Teflon cap and the interior of the NPT valve. These washings were added to the reactor. Solids were suspended in the DCM washings and then filtered to isolate the solids. The reactor was washed enough times to remove all residue. The solids were washed ~3× with 5 mL portions of DCM, then dried at ~1 Torr overnight. This product was assigned the “solids fraction”. GPC analysis was carried out for this product fraction. The DCM washings were collected, and the DCM was removed under reduced pressure overnight (~1 Torr). The DCM-soluble hydrocarbons are assigned as “DCM extract”. Note that some volatile liquid hydrocarbons (CS–C7) are lost during DCM removal. However, we find that <5 wt% of the total product mass is lost. Approximately 10 mg of the DCM extract fraction was added to ~1 mL DCM for GC/MS analysis. Unaccounted-for mass is assigned to the “volatiles” fraction, and the presence of light hydrocarbons is confirmed via GC-FID. The percent conversion of a polylefin hydrogenolysis reaction is defined as the mass of “volatiles” and “DCM extract” produced as a percentage of the initial polylefin mass. Uncertainty in polymer hydrogenolysis products mass was estimated to be 20 mg (1–2% of initial polymer mass) and was carried over into calculating polymer hydrogenolysis activities.

Synthesis of AIS/ZrH(Np), AIS/ZrD(Np) and AIS/Zr(alkyl)2 (Pentane-treated AIS/ZrH(Np))

In the glovebox, AIS/ZrNp2 (200 mg) was added to a dry 75 mL heavy-walled glass pressure reactor. The reactor was sealed, interfaced to a high pressure/high vacuum line, evacuated, then charged with 1 atm H2. The reactor was heated to 150 °C for 5 min, then evacuated. A color change from pale yellow to colorless was observed. This cycle was repeated once more. The solid was then used as needed for further reactions or measurements. AIS/Zr(H/2) was synthesized in an analogous fashion as AIS/ZrH(Np), using D2 in place of H2. To synthesize AIS/Zr(alkyl)2, pentane (~0.5 mL) was vacuum transferred into a 75 mL pressure reactor containing AIS/ZrH(Np) (200 mg) on a high-pressure/high vacuum line. The reactor was heated at 150 °C for 30 min. In the first 30 s of heating, a color change from colorless to pale yellow was observed. The AIS/Zr(Np)–pentane sample has the following bond configuration, as determined by EXAFS: three Zr–O bonds with lengths 1.97(1), 2.16(1), 2.16(1) Å, and two Zr–C bonds with lengths 2.37(1), 2.45(1) Å.

Data availability
Computational data and code used in this study have been deposited in the iochem-BD database under the following https://doi.org/10.19061/iochem-bd-6-182. All additional information is available in the supplementary materials.

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Author contributions

A.H.M., Y.K., T.J.M. conceived the concepts and designed experiments. A.H.M. performed the experiments with aid from Y.K. A.M. performed the DFT analysis. Q.M. performed the XANES/EXAFS experiments. A.D. analyzed the XANES/EXAFS data with guidance from M.J.B. Y.K., A.H.M., T.J.M. performed the experiments with aid from Y.K. A.M. performed the experiments with aid from Y.K. A.M. performed the DFT analysis. Q.M. performed the XANES/EXAFS experiments. A.D. analyzed the XANES/EXAFS data with guidance from M.J.B. Y.K., A.H.M., T.J.M. wrote the manuscript.

Competing interests

The authors declare they have no competing interests.

Additional information

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