Catalytic carbon-carbon bond cleavage and carbon-element bond formation give new life for polyolefins as biodegradable surfactants

A new catalytic transformation of saturated hydrocarbons involving carbon–carbon bond cleavage and aluminiation is developed and investigated for the upcycling conversion of polyolefins into biodegradable fatty alcohols and fatty acids.

Uddhav Kanbur, Guiyan Zang, Alexander L. Paterson, ..., Frédéric A. Perras, Pingping Sun, Aaron D. Sadow
sadow@iastate.edu

Highlights
Catalytic C–C bond cleavage chops and functionalizes aliphatic hydrocarbons
Sustainable conversion of polyolefins into biodegradable, value-added fatty alcohols
Metalative cleavage employs earth-abundant zirconium catalysts and aluminum reagents

Kanbur et al., Chem 7, 1347–1362
May 13, 2021 © 2021 Elsevier Inc.
https://doi.org/10.1016/j.chempr.2021.03.007
Catalytic carbon-carbon bond cleavage and carbon-element bond formation give new life for polyolefins as biodegradable surfactants

Uddhav Kanbur,1,2 Guiyan Zang,3 Alexander L. Paterson,1 Puranjan Chatterjee,1,2 Ryan A. Hackler,4 Massimiliano Delferro,4 Igor I. Slowing,1,2 Frédéric A. Perras,1 Pingping Sun,3 and Aaron D. Sadow1,2,5,*

SUMMARY
Catalytic methods that introduce functional groups via carbon–carbon bond cleavage steps have typically been limited to moieties activated by strain or by directing groups, with few transformations engaging the bonds of only sp3-hybridized carbon atoms in saturated hydrocarbons. Here, we report the conversion of catenated carbon chains in polyolefins, which currently represent >50% of discarded plastics, into shorter aliphatic alkylaluminum species via a sequence of zirconation via C–H bond activation, β-alkyl elimination for carbon–carbon bond cleavage, and heterobimetallic alkyl group exchange for carbon–aluminum bond formation. The versatility of aliphatic alkylaluminum species is exemplified by their subsequent conversion into high-value fatty acids or alcohols, which have applications as biodegradable surfactants and detergents. A techno-economic analysis indicates that fatty alcohols produced from discarded polyolefins are cost competitive with conventional syntheses. Thus, this process could ameliorate economic and environmental challenges of the plastic-waste crisis.

INTRODUCTION
C–H bond metalations, in which a hydrogen atom is replaced by a metal center, have revolutionized syntheses by reducing or eliminating requirements for specific and limiting chemical functional groups.1–3 In these metalations, the carbon-based molecular framework of the organic reactants is preserved in the functionalized products. An even wider range of starting materials could be leveraged by methods that concurrently alter the carbon-based skeleton of organic molecules and introduce new functional groups. With such transformations, for example, natural resources that contain structural components of the desired products would become available for chemical manufacturing, or framework reconstructions could increase late-stage structural diversification during multistep syntheses. C–C bond metalations, in which a metal center replaces a specific hydrocarbyl moiety, would enable these framework functionalization reactions. Current methods that install a metal center by breaking a carbon–carbon bond, however, are limited to positions activated either by thermodynamically weakened bonds or directing functional groups (Figure 1A).4–7 On the other hand, established C–C bond cleavages involving only sp3-hybridized carbon centers generally do not provide new carbon–heteroatom bonds. For example, alkane metathesis (Figure 1B) alters chain lengths without introducing new functional groups.8,9 Likewise, hydrogenolysis of carbon–carbon bonds in hydrocarbons, catalyzed by heterogeneous platinum-group nanoparticles10,11 or air-sensitive early transition metal hydrides,12,13 provides shorter alkane products.
Molecular skeleton restructuring transformations could be useful, for instance, in the deconstruction of polymers for which there are growing environmental and socio-economic concerns. Conventional technologies, such as mechanical recycling through melt-processing, are insufficient to fully address this global problem. Chemical conversion of polymers have been proposed as an alternative strategy that could provide a second life for the catenated chains of used plastics. For example, polyolefins may be transformed into liquid fuels by pyrolysis or hydrocracking, polyesters may be chemically recycled via monomers, plastic-to-plastic transformations can upcycle used materials into new ones, and discarded plastics can serve as feedstocks for value-added chemical products. Alkane cross-metathesis, noble-metal-nanoparticle catalyzed hydrogenolysis, and surface-supported zirconium-hydride-catalyzed hydrogenolysis noted above, have been adapted to transform polyolefins into waxes, oils, lubricants, or alkylaromatics.

Figure 1. Catalytic methods for carbon–carbon bond cleavage

(A) Functional groups may be added at thermodynamically activated or kinetically preferred positions.

(B and C) Saturated hydrocarbons in small molecules and polymers may be shorted by alkane metathesis (B) or nanoparticle or early-metal hydride-catalyzed hydrogenolysis (C) without introduction of new functionality.

(D) Carbon–carbon bond cleavage and aluminum–carbon bond formation is catalyzed by surface-supported organozirconium species.

1US DOE Ames Laboratory, Iowa State University, Ames, IA 50011, USA
2Department of Chemistry, Iowa State University, Ames, IA 50011, USA
3Systems Assessment Center, Energy Systems Division, Argonne National Laboratory, Lemont, IL 60439, USA
4Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA
5Lead contact
*Correspondence: sadow@iastate.edu
https://doi.org/10.1016/j.chempr.2021.03.007
Of the existing methods, only the oxidative degradation of polyolefins provides useful functionalized small molecules, such as in the conversion of high density polyethylene (HDPE) into a mixture of short \( \alpha,\omega \)-diacids (e.g., \( \text{HO}_2\text{C(CH}_2)_n\text{CO}_2\text{H; } n = 2–5 \)), whose selectivity is governed by the rules of radical chemistry. These reactions, as well as pyrolytic approaches, are currently moving toward commercial practice for the conversion of polyolefins. Catalytic C–C bond metatation reactions, which provide versatile organometallic intermediates, could benefit from catalyst-controlled selectivity to enable upcycling transformations to narrow distributions of long-chain chemicals.

Intermediate-length chain-alkylaluminum species are high among desirable targets for polymer deconstruction processes because these organometallics, conventionally synthesized using the Ziegler process, can be converted into fatty alcohols and acids through established methods. The heteroatom-functionalyzed species are biodegradable and, if produced from discarded polyolefins, would provide an environmentally friendly end-of-life for some plastics. In addition, the hydrido- or organoaluminum reagents to be employed in such transformations are further advantaged because aluminum is widely available as the most abundant metal (8.2% as an oxide) in the earth’s crust, and it is readily converted (or recycled) from its oxide to metal to organoaluminum species in atom-economical, optimized processes performed on a large scale.

We envisioned that organotransition-metal species, generated as catalytic intermediates by cleavage of C–C bonds in saturated hydrocarbons, could undergo metathetical exchange with organo- or hydridoaluminum species, to create the new intermediate-length chain hydrocarbyl-aluminum species. Such alkyl group metathetical steps are established in carboalumination and hydroalumination of alkenes and as chain-transfer steps in chain-shuttling block copolymerizations of ethylene and \( \alpha \)-olefins. These processes commonly engage organozirconium catalysts. Moreover, coordinatively unsaturated zirconium sites, including surface-supported zirconium hydride in catalytic polyolefin hydrogenolysis, are known to break C–C bonds by \( \beta \)-alkyl elimination. The related \( \beta \)-allyl elimination and organozirconium/hydridoaluminum exchange are proposed in polybutadiene deconstruction and alumination, catalyzed by \( \text{Cp}_2\text{ZrHCl} \) (Schwartz’s reagent), which attaches to the chain by hydrozirconation rather than C–H bond metatation.

Here, we report the catalytic C–C bond alumination of sp\(^3\)-hybridized carbon in aliphatic hydrocarbons, leveraging C–H bond activation and \( \beta \)-alkyl elimination steps of surface organometallic zirconium chemistry. Our studies have focused on identifying effective catalysts and aluminum reagents, as well as understanding their effects upon the elementary steps involved in reactions through conversions of polyethylene into fatty aliphatic alkylaluminum species.

**RESULTS**

**Design of carbon–carbon bond alumination**

The first experiments employed \( \text{Zr(CH}_2\text{CMe}_3)_2@SiAlO}_x \) (2.7 wt % Zr, 0.30 mmol Zr/g), which was prepared by grafting \( \text{Zr(CH}_2\text{CMe}_3)_4 \) onto partially dehydroxylated silica-alumina (0.38 mmol SiOH/g; 9.3 wt % Al; 182 m\(^2\)/g; see Figure S89) in pentane (see Supplemental experimental procedures). The surface species contains an average of two neopentyl groups per zirconium center, as determined by elemental analysis using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and protonolytic titration. Melted HDPE and \( \text{AlBu}_3 \) (~10:1 by weight) react in the presence of this precatalyst over 12 h at 150°C to give, after flowing...
dry air through the reactor and extraction with methylene chloride, an oil containing fatty alcohols and alkanes in a nonoptimized 31% yield (based on initial HDPE mass, Scheme 1). Fatty alcohols in the product mixture corresponded to O₂-quenched organometallic species, including alkylaluminum and any active alkylzirconium intermediates, whereas hydrocarbons were present in the reaction mixture prior to quenching. Thus, the combination of Zr(CH₂CMe₃)₂@SiAlOₓ and AlBu₃ mediates the desired carbon–carbon bond cleavage and carbon–aluminum bond formation in aliphatic hydrocarbons.

The isolated reaction products were analyzed by infrared (IR) and 1D and 2D solution-phase nuclear magnetic resonance (NMR) spectroscopy, matrix-assisted laser desorption ionization time of flight-mass spectrometry (MALDI-TOF-MS), and gas chromatography mass spectrometry (GC-MS). The first evidence of alcohol products in the isolated oils was provided by broad signals in the IR spectrum at 3,430 and 1,090 cm⁻¹ that were characteristic of νO-H and νC-O stretching bands (Figure S4). These assignments were further supported by MALDI-TOF-MS analysis, which detected functionalized monoalcohols from C₁₃H₂₇OH up to C₆₄H₁₂₉OH directly and aliphatic hydrocarbons as ¹⁰⁷/¹⁰⁹Ag⁺ adducts (see Figure S5). In addition, quantification of the components by GC-MS analysis revealed fatty alcohols from C₁₂–C₂₀ and long-chain hydrocarbons C₁₉–C₃₀ compose only 6% of the oil, by mass. Notably, we did not detect signals corresponding to alkenes in IR, MALDI-TOF-MS, GC-MS, or NMR spectra of the products (see below).

Analysis of 1D and 2D NMR spectra provided additional insight into the products’ structural features. The ¹H NMR spectrum of the oil contained resonances at ca. 3.6 ppm, assigned to CH₂OH in alcohols (Figure S1), which correlated with the aliphatic hydrocarbon signals at 1.6 ppm in a COSY experiment (Figure S2). The 3.6 ppm resonance also correlated with ¹³C NMR signals at 60–70 ppm in a phase-sensitive ¹H-¹³C heteronuclear single quantum coherence (HSQC) spectroscopy experiment (Figure S3). These cross-peaks appear with the same phase as those at 30 ppm, assigned to the CH₂ signals from the polyethylene backbone, and the phase opposite to that of cross-peaks at 13 ppm assigned to methyl groups. These data indicate that the detectable alcohol groups in the oil are primary, leading to the conclusion that the direct products of C–C bond cleavage in HDPE are terminal organometallic species.

Because all molecules in the oil are either monoalcohols or alkanes (i.e., there are either one or zero OH groups per molecule), as shown by the MALDI-TOF-MS
analysis, the fraction of molecules containing functional groups (in this case, OH) is equal to the fractional number of functional groups per molecule (#FG). The #FG were calculated as the difference between the number of end groups (#EG) on a chain and the number of methyl chain ends (#CH₃). The #EG is equal to the sum of the two end groups in a linear chain and the end groups created by each of the branching points, and the number of branch points is equal to the number of methine groups (#CH), giving Equation 1 for calculating the fraction number of functional groups per molecule:

\[
#FG = #EG - #CH₃ = (2 + #CH) - #CH₃ \quad (\text{Equation 1})
\]

Using integration of the assigned ¹H NMR spectrum, the fact that all alcohols are terminal, and assuming that CMe₂ groups and cyclic species are insignificant, this oil is estimated to contain a 7:3 ratio of monoalcohol:alkane. The absolute yield of alcohols corresponds to ca. 50% of the total valence available from the AlBu₃ (i.e., 1.5 fatty alkyl chains per aluminum). In addition, 40% of the methyl groups present in the oil are bonded to methine carbons, and the remaining methyl groups are bonded to methylene carbons (chain or long branch ends). These MeCHRR' moieties may be formed via 1,2-insertion of an α-olefin into a metal-alkyl, which subsequently metalates another polymer chain, or as a part of a methylalumination process (Me₃C-CH₂Al species are known to react by β-methyl elimination).³³

At 200°C, the Zr(CH₂CMe₃)₂@SiAlOₓ-catalyzed reaction of HDPE and 10 equiv of AlBu₃ gave a higher yield of oils (40%) (Table 1, entry 2) after 12 h. A MALDI-TOF-MS revealed shorter chains (a C₃₄-centered distribution) (Figure S10) compared with the products from the experiment at 150°C. The synthetic versatility of the alkylaluminum products was demonstrated in HDPE deconstruction reactions quenched with methanol, I₂, or CO₂ (Table 1, entries 4–6) that gave hydrocarbons, or mixtures containing alkyl iodides or fatty acids, respectively. As expected, similar C₃₂–C₃₄-centered distributions of chains (see MALDI-TOF-MS of fatty acids in Figure 2) are obtained with protonolytic, oxidative, or electrophilic quenching agents, indicating that identical fatty alkylaluminum species are intermediates, and the quenching agent does not affect the product chain length. We also note that this catalytic system transforms postconsumer HDPE from a supermarket bag, which was otherwise untreated, as well as isotactic polypropylene (iPP) (Table 1, entries 11 and 12), which also provides functional-group-containing oils. Note that CH metalation of methyl groups in iPP, followed by β-alkyl elimination, readily deconstructs the polymer backbone.

Effects of aluminum reagents
On the basis of these initial results, and leveraging the analytical methods adapted to characterize the composition and structure of a distributions of functionalized chains, we investigated the effects of aluminum reagents on catalytic carbon–carbon bond cleavage and alumination in conversions of polyethylene. Essentially identical yields were obtained after 24 h of continuous heating or upon addition of a second portion of AlBu₃ after 12 h, suggesting that the zirconium catalyst was deactivated during the first portion of the reaction. Experiments with more AlBu₃ (50 equiv relative to Zr) gave only minimal amounts of oil (3%). Together, these experiments suggest that the aluminum reagent at higher quantities is involved in catalyst deactivation steps.³⁸ Improved conversion of HDPE was instead accomplished by adding portions of Zr(CH₂CMe₃)₂@SiAlOₓ, and AlBu₃ every 12 h. Polymer was not observed after three reaction cycles with a total oil yield of 84%.

Main-group alkyl and hydride reagents influence catalytic alkene polymerizations and could also affect these deconstruction reactions. The trend of reactivity of a
series of main-group compounds in this Zr(CH₂CMe₃)₂@SiAlOₓ-catalyzed polyethylene conversion process, in terms of yields of oils, is AlH₃ > AlBu₃ > AlPh₃ > AlEt₃ > AlMe₃ > HAI Bu₂ (DIBAL-H) > HAIMe₂ > ZnEt₂. The Al reagents which react by hydride transfer, namely AlH₃ and AlBu₃, give higher yields of functionalized chains than reagents that only transfer organic groups such as AlMe₃. Several of these experiments also provide evidence for metalation and carboalumination steps that are part of the proposed reaction pathway (see below). In the absence of aluminum reagents under otherwise identical conditions, only minor amounts of light alkenes and alkanes are detected in the reaction mixture.

The most effective co-reactant for Zr-catalyzed deconstruction of HDPE was AlH₃, the reaction of which provided oil in a yield (42%) comparable with the reaction with AlBu₃ and a significantly higher proportion of alcohol chains (89%) in the oil product. Similar ranges of CₙH₂n+₁OH (30 ≤ n ≤ 44) species were observed in the MALDI-TOF-MS spectra (Figure S10 and S10.5) of oils obtained in otherwise equivalent reactions using AlH₃ and AlBu₃ at 200°C. Triethylaluminum (AlEt₃) was

| Entry | Initial polymer mass (g) | Conditions | Yield | % functionalized chains |
|-------|--------------------------|------------|-------|-------------------------|
|       |                          | AliBu₃, T (°C) | Mass (g) | % versus PO |
| 1     | 0.63                     | 150         | 0.19  | 31          | 71            |
| 2     | 1.00                     | 200         | 0.4   | 40          | 68            |
| 3     | 1.00                     | 200         | 0.84  | 84          | 66            |
| 4     | 1.00                     | 200         | 0.38  | 38          | N/A           |
| 5     | 0.54                     | 200         | 0.23  | 43          | 68            |
| 6     | 0.55                     | 200         | 0.20  | 36          | 75            |
| 7     | 0.51                     | 150         | 0.13  | 25          | 39            |
| 8     | 0.60                     | 200         | 0.15  | 24          | 54            |
| 9     | 0.64                     | 200         | 0.19  | 29          | 66            |
| 10    | 0.52                     | 200         | 0.22  | 42          | 89            |
| 11    | 0.60                     | 200         | 0.19  | 31          | 60            |
| 12    | 1.00                     | 200         | 0.27  | 27          | N/A           |
|       |                          | AliEt₃, T (°C) | Mass (g) | % versus PO |
| 13    | 0.60                     | 200         | 0.21  | 34          | 51            |
| 14    | 0.35                     | 200         | 0.17  | 49          | 62            |
| 15    | 0.85                     | 200         | 0.51  | 60          | 67            |
|       |                          | AliH₃, T (°C) | Mass (g) | % versus PO |
| 16    | 1.00                     | 200         | 0.35  | 35          | 85            |
| 17    | 0.41                     | 200         | 0.13  | 33          | 82            |

PO, polyolefin; N/A, not applicable.

*Standard conditions: 21 kg HDPE/mol Zr, Al:Zr = 10:1, 150°C–200°C, 12 h, followed by O₂ quench to give fatty alcohols. Data in support of this table is given in Figures S1–S17.

**HDPE: Mₙ = 6.2 kDa, Mₙ = 38.6 kDa, D = 6.2.**

†% Yield = mass of oil/mass of PO.

‡3 portions of Zr(CH₂CMe₃)₂@SiAlOₓ/AlBu₃ were added over 36 h.

*Quenched with MeOH to give saturated hydrocarbon products.

†Quenched with I₂ to provide long-chain alkyl iodides.

‡Quenched with CO₂ to form fatty acids.

‡Postconsumer HDPE: Mₙ = 5.3 kDa, Mₙ = 105 kDa, D = 19.8.

*IP: Mₙ = 37.4 kDa, Mₙ = 117.6 kDa, D = 3.2. Quantitative estimation of functional group analysis of the product is not possible due to quaternary carbon centers.

‡Performed under dynamic vacuum.
less effective for carbon–carbon bond cleavage than AlBu3 or AlH3 in the presence of Zr(CH2CMe3)2@SiAlOx as precatalyst, affording oils in 23% yield after 12 h at both 150°C and 200°C. The structure, HO-CH2-CH(CH2CH3)-polymer chain, identified through a 1H-1H COSY experiment (Figure S34), was the dominant alcoholic species, based on the 1.53:1 ratio of integrated signals of (CH)–CH2–CH3 to CH2–OH (Figure S33). The fraction of molecules containing OH, as calculated using Equation 1, was 0.39. Thus, AlEt3 was less active than AlBu3 and also less effective for introducing aluminum into the products, giving the highest percentage of alkanes of all reactive aluminum reagents (see Discussion). A higher yield of oil product (29% by mass after work-up with O2) from the catalyzed reaction of HDPE and AlPh3 at 200°C compared with AlEt3 was partially affected by the added mass accompanied by formation of aromatic-containing species, identified by 1H and 13C NMR spectroscopy, and MALDI-TOF-MS (Figures S9.1–S9.6). Treatment of HDPE with either ZnEt2 or AlMe3, which are often effective in coordinative chain-transfer polymerization,54,55 or aluminum hydride reagents HAliBu2 and HALMe2 did not provide fatty alcohol oils after work-up.

Catalytic materials
A control experiment lacking zirconium, in which partially dehydroxylated SiAlOx, AlBu3, and HDPE were heated at 200°C for 12 h, returned the polymer with little change to its molecular weight (Mw = 5.8 kDa) and trace amounts (<2%) of trimerized isobutylene from AlBu3 thermolysis.56 Although acid sites on SiAlOx (or even weaker silanols on SiO2) mediate degradation of HDPE at 200°C,57 AlBu3 reacts to cap the few surface silanol sites58,59 and blocks acid-promoted thermolysis to favor zirconium-catalyzed pathways. In addition, negligible amounts of oil are obtained from catalytic deconstruction/alumination experiments in which Zr(CH2CMe3)2@SiAlOx is pretreated with H2 to generate hydridozirconium species as the precatalyst.

We initially tested Zr(CH2CMe3)2@SiAlOx because its surface hydrides are reported to be more active for propane metathesis and polyolefin hydrogenolysis than the
silica-supported analogs. Our direct dynamic nuclear polarization (DNP)-enhanced \(^{17}\)O\(^{27}\)Al transfer of population double-resonance (TRAPDOR) NMR experiments, however, revealed that the Zr is not in close proximity to Al centers in the precatalyst (Figure S96). More specifically, while the oxide \(^{17}\)O sites predictably dephased following \(^{27}\)Al irradiation, indicating the presence of O-Al linkages near the surface, the \(^{17}\)O sites bound to Zr did not, revealing that the Zr coordinates exclusively to silanols in the precatalyst with the structure \(\equiv\text{SiO}_2\text{Zr(CH}_2\text{CMe}_3)_2\) and not by reacting at \(\equiv\text{Si–OH–Al}\) Brønsted acid sites.

We investigated a silica-supported zirconium catalyst based on this spectroscopic result. An aerosil silica-supported zirconium catalyst, Zr(CH\(_2\)CMe\(_3\))\(_2\)@SiO\(_2\), after heating with HDPE and Al\(_i\)Bu\(_3\) for 12 h at 200 °C, provided an alcohol-containing oil in nearly equivalent yield (35%) as the silica-alumina-supported catalyst. Moreover, the oil was composed of approximately 85% alcohols and only 15% alkanes. The Zr(CH\(_2\)CMe\(_3\))\(_2\)@SiO\(_2\)-catalyzed reaction with AlEt\(_3\) provided the oil product in similar single-pass yield (32%) and high alcohol content (82%), as a contrast with the silica-alumina supported zirconium catalyst. These reactions afforded alcohol species with a normal, ca. C\(_{35}\)-centered distribution of monoalcohols, as detected by MALDI-TOF-MS (Figures S16.5 and S17.5, respectively). The similarly high reactivity of catalysts supported on silica and silica-alumina may be attributed to the known surface alumination and subsequent incorporation of aluminum centers into silica framework sites in reactions of excess Al\(_i\)Bu\(_3\) and SiO\(_2\). In fact, trace amounts of ethylsilane species were detected in GC-MS and NMR spectra of the reaction products, which was consistent with aluminum substitutions for silicon occurring in the silica support framework during the catalytic reaction. This in situ alumination of the silica support could influence the reactivity of the active species generated from the Zr(CH\(_2\)CMe\(_3\))\(_2\)@SiO\(_2\) precatalyst. Such an effect would not be available in alkylaluminum-free hydrogenolysis reactions catalyzed by surface-supported hydridozirconium, leading to distinct activity for zirconium supported on the two oxides.

The silica- or silica-alumina-supported neopentylzirconium, as well as the \(\equiv\text{SiO}_2\text{ZrH}\) catalyst for polyethylene hydrogenolysis, are exceedingly sensitive to irreversible reactions with air and moisture to give deactivated materials. Thus, small amounts of protic or oxidative impurities in the polyethylene reactant could have an outsized effect upon catalytic performance. Because the alkylaluminum reactant can serve as an alkylating agent for converting alkoxyzirconium into alkylzirconium surface species, some poisoned sites could also be reactivated under catalytic conditions. In this context, we note that the polyolefin reactants used in this study, although clean and dry, were essentially used as received and did not undergo exhaustive purification prior to use. Moreover, convenient precatalysts for HDPE deconstruction should be tolerant of air and moisture. Remarkably, Zr(CH\(_2\)CMe\(_3\))\(_2\)@SiO\(_2\) exposed to O\(_2\) was catalytically active for the reaction of HDPE and Al\(_i\)Bu\(_3\) and gave an oil in 34% yield with ca. 50% selectivity to alcohols. This air-exposed precatalytic material Zr(OCH\(_2\)CMe\(_3\))\(_2\)@SiO\(_2\) can also be activated by AlH\(_3\), and the reaction with HDPE afforded a higher yield (49%) and higher selectivity to alcohols (62%). Thus, alkoxyzirconium species are viable precatalysts for carbon–carbon cleavage and alumination.

**Technoeconomic analysis**

These polyolefin deconstruction and heterofunctionalization reactions will enable the development of incipient plastic upcycling and manufacturing efforts that are either integrated into materials recovery facilities on a small scale or centralized.
over fewer, larger-scale facilities. A technoeconomic analysis (TEA) of a conceptual centralized plant (see supplemental experimental procedures; Figure S94) was carried out to process 250 metric tons (MT) of PE/day, at 90% utilization, and produce ca. 71 MT fatty alcohol sulfate/day, as well as valuable paraffinic lubricant co-products. In the design, the expenses associated with the Zr catalyst and alkylaluminum reagents are recouped by fully separating and recovering the former and by reselling the latter as AlCl₃ co-products (see Tables S1–S3). The estimated minimum product market price for the resultant surfactant (C₄₀H₈₁OSO₃Na) is US$ 3.4/kg (Figure S95), which is comparable to the US$ 1–3/kg current market price of sodium lauryl sulfate (from C₁₂ alcohol).

Straightforward production of eicosanol (C₂₀) and docosanol (C₂₂), which are considerably more valuable than C₁₂ alcohol (see Table S4), could further motivate collection and processing of used polyethylene. Finally, we note that the longer functionalized chains, uniquely inexpensive from this polymer deconstruction/alumination process, could find new applications for upcycled polyolefins. The fatty alcohol or fatty acid products obtained from catalytic deconstruction/alumination complement the short-chain diacids formed from oxidative polymer degradations, unsaturated species from thermal or pyrolytic processes, or hydrocarbons from hydrogenolysis or alkane metathesis. Given the massive amounts of polyolefins that are discarded each year, this complementarity, as well as the potential new applications of long-chain fatty alcohols and acids which are inaccessible by traditional synthetic means, could benefit the implementation of this or related transformations in the incipient practice of upcycling plastics into new, value-added products.

DISCUSSION
Evidence for sequence of elementary steps
This Zr-catalyzed polyethylene deconstruction to produce long-chain alkylaluminum species likely follows the sequence of elementary steps shown in Scheme 2. First, the polymer backbone and a surface-grafted alkyl or hydridozirconium species react via methylene C–H bond activation (1) to generate a midchain polymerylzirconium species. Then, β-alkyl elimination (2) from the midchain polymerylzirconium results in carbon–carbon bond cleavage to give a terminal olefin and a new oligomerylzirconium species C. Finally, chain transfer to aluminum (3) occurs via heterobimetallic alkyl group metathesis of the alkylzirconium with an alkyl or hydridoaluminum species and carboalumination or hydroalumination of the in situ generated olefin by AlR₃ results in a new aluminum–carbon bond.

Observations described below, made in the course of catalytic experiments, provide support for the reaction sequence shown in Scheme 2. First, evidence for metatation by alkylzirconium species in step 1 is provided by the reaction by-products. Neopentane (CMe₄) is detected in the reactor headspace within the first 15 min of experiments catalyzed by Zr(CH₂CMe₃)₂@SiAlOₓ, regardless of the organoaluminum reagent used, suggesting that the polymer is metalated by a Zr-CH₂CMe₃ species. In a control experiment, CMe₄ was not detected in the reaction of HDPE with Zr(OCH₂CMe₃)₂@SiAlOₓ and AlBu₃. Thus, CMe₄ formation is associated with metatation by neopentylzirconium rather than resulting from reaction of neopentylaluminum species and/or polymer hydrogenolysis. Other organozirconium intermediates also likely react with polymer chains, via metatation, to give midchain polymerylzirconium species. For example, benzene is observed in reactions involving AlPh₃ (prior to work-up with O₂), supporting the idea that phenylzirconium intermediates react with hydrocarbons by metatation. Oligomerylzirconium species (C), generated
by β-alkyl elimination of B, also can react with polymer chains via metalation, short circuiting the chain alumination process and leading to the observed molecular aliphatic hydrocarbon products.

Surface zirconium hydride species, formed by ligand exchange or hydride transfer reactions of alkyl zirconium and hydridoaluminum or isobutylaluminum, respectively, also likely are involved in polymer metalation of step 1. Several observations support the idea that aluminum reagents generate zirconium hydrides. First, hydridoaluminum species are formed from Al\textsubscript{iBu\textsubscript{3}} at high temperatures. Second, the reaction of Zr(CH\textsubscript{2}CMe\textsubscript{3})\textsubscript{2}@SiAlO\textsubscript{x} and Al\textsubscript{iBu\textsubscript{3}} at 150°C for 4 h provided a material that contained a band in a diffuse reflectance infrared Fourier transform (DRIFT) spectrum at 1,623 cm\textsuperscript{-1} assigned to a ν\textsubscript{Zr–H} (Figure 3) on the basis of labeling experiments and comparison to literature reports. In particular, this signal disappeared upon treatment with D\textsubscript{2} (the signal for presumed ν\textsubscript{Zr–D} is not resolved from Si/Al–O bands) and reappeared upon exposure to H\textsubscript{2} (Figure 3). The DRIFT spectrum of SiAlO\textsubscript{x} treated with Al\textsubscript{iBu\textsubscript{3}}, in contrast, was unchanged by reaction with D\textsubscript{2}. Third, during the catalytic HDPE deconstruction and alumination reactions involving Al\textsubscript{iBu\textsubscript{3}}, isobutylene was the most abundant species in the gas phase (along with a small, but detectable amount of isobutane), which was also consistent with the generation

**Scheme 2. Plausible sequence for polyethylene deconstruction and alumination**

Possible sequence of elementary steps involved Zr-catalyzed polyethylene deconstruction into long-chain alkylaluminum species, namely (1) metalation of the polymer backbone via C–H bond activation by a grafted alkyl- or hydridozirconium species A, (2) β-alkyl elimination from a midchain polymerylzirconium B, resulting in C–C bond cleavage to give a terminal olefin and a new oligomerylzirconium species C, (3) alkyl group metathesis of the oligomerylzirconium with an alkyl or hydridoaluminum species; and (4) carboalumination of an in situ generated olefin by Al\textsubscript{R\textsubscript{3}} resulting in a new C–C bond.
of hydridozirconium species. The reaction of Zr(CH$_2$CMe$_3$)$_2$@SiAlO$_x$ and Al$i$Bu$_3$ at room temperature also produced isobutylene (Figure S92), although the Zr–H band in the DRIFT spectrum was very weak under that condition. Finally, hydride-generating aluminum reagents (AlH$_3$ and Al$i$Bu$_3$) provided higher yields of oils than reactions with alkyl (AlEt$_3$) or aryl (AlPh$_3$) transfer reagents, which may reflect increased rates of methylene C–H bond activation by hydridozirconium compared with alkyl or arylzirconium.

Midchain polymerylzirconium species B are cleaved via β-alkyl elimination, leading to polymer deconstruction into a shorter terminal oligomerylzirconium C and vinyl-terminated chain fragments in step 2. The oligomerylzirconium reacts with AlR$_3$ via heterobimetallic alkyl group exchange or hydride transfer to produce the oligomerylaluminum product and regenerate the alkyl- or hydridozirconium catalyst in step 3. Catalytic hydroalumination or carboalumination of the vinyl-termination polymer fragment, via insertion into alkyl- or hydridozirconium and chain transfer, affords β-branched (R$_2$Al-CH$_2$CHR–) or linear (R$_2$Al-CH$_2$CH$_2$) aluminum terminated chains in step 4. These species were detected in the products of AlEt$_3$ and AlPh$_3$ and analyzed by 1D and 2D NMR spectroscopy. Thus, all functional groups terminate the chains as a consequence of the β-alkyl and chain-transfer mechanistic sequence.

We have ruled out at least one other sequence of elementary steps that could account for the observed fatty alkylaluminum products. Specifically, terminal polymerylzirconium species could also react by β-alkyl elimination to generate ethylene (Figure S93). This thermodynamically unfavorable step, the microscopic reverse of ethylene insertion during polymerization, could be coupled to an exothermic, catalytic ethylene oligomerization process that provides the medium-length chains of the alkyl aluminum or alkane products. Independent oligomerization or

---

**Figure 3.** DRIFT spectra of ZrH@SiAlO$_x$

(A) Room temperature DRIFT spectra of (A) Zr(CH$_2$CMe$_3$)$_2$@SiAlO$_x$ + Al$i$Bu$_3$ heated at 150°C for 2 h, washed with anhydrous pentane and dried in vacuo.

(B) D$_2$ gas (1 atm) passed over sample (A) at 70°C for 30 min.

(C) H$_2$ gas (1 atm) passed over sample (B) at 70°C for 30 min. Compare with DRIFT spectrum of Zr(CH$_2$CMe$_3$)$_2$@SiAlO$_x$ in Figure S90.
polymerization experiments involving small amounts of ethylene, Zr(CH₂CMe₃)₂@SiAlOₓ, and AlBu₃ did not give fatty-alcohol-range molecular weight species. Thus, we ruled out a pathway to oils involving HDPE depolymerization to ethylene followed by Ziegler Aufbau-type oligomerization, although the individual elementary steps, namely ethylene formation and reinsertion, were not ruled out by this experiment.

Related side reactions, such as alkene insertion, are likely also a small part of the catalytic mechanism. In addition, the oligomerylzirconium intermediates can react with small molecules, such as H₂ or benzene, through bond metathesis steps to form hydrocarbons. Accordingly, high alkane content was observed with the catalytic systems Zr(CH₂CMe₃)₂@SiAlOₓ/AlPh₃ (ca. 55%) and Zr(OCH₂CMe₃)₂@SiAlOₓ/AlBu₃ (ca. 50%). This influence of small molecules was further examined by removing the volatile species, in reactions of HDPE and AlH₃ in the presence of Zr(OCH₂CMe₃)₂@SiAlOₓ under continual evacuation (Table 1, entry 15). Under these conditions, a high single-pass yield (60%) was obtained, even though the mass of the reaction mixture decreased by 21%. MALDI-TOF-MS analysis of the oil formed under these conditions revealed that increased amounts of lower-molecular-weight alcohols, from C₂₀H₄₁OH to C₃₈H₇₇OH, were formed under vacuum than in a sealed vessel. This oil contained comparable fraction of alcohol molecules (~67%) as the experiment under N₂. Clearly, the removal of small molecules from the reaction mixture slows undesired bimolecular processes relative to unimolecular chain cleavage by β-alkyl elimination. However, the relative rate of alkylaluminum formation compared with alkane production is not affected by performing the reaction under a dynamic vacuum, probably because the effective concentrations of AlR₃ and CH bonds, leading to the two kinds of products, are not significantly altered by removing volatile species.

In conclusion, the combination of β-alkyl elimination and heterobimetallic alkyl group metathetical exchange at surface-immobilized organozirconium sites provides a valuable method to install reactive groups and reconstruct the carbon skeleton of organic molecules, without the need for prior activation or directing groups. The alkylaluminum reagent can activate air-stable alkoxyzirconium species to generate highly air-sensitive hydridozirconium active sites, which are also inoculated by the alkylaluminums against poisoning. We are currently investigating the performance of commercially available, air-stable catalyst precursors to further simplify manipulations as well as sites containing robust ancillary ligands to affect the rates of β-alkyl elimination and chain-transfer steps. The relative rates of these steps affect the average carbon-chain lengths of the products, advantageously allowing catalyst-controlled mechanisms to be optimized to obtain desired products. Both AlBu₃ and AlH₃ react with alkyl and alkoxyzirconium species to generate surface zirconium hydrides. Moreover, both the catalysts and reactants are based upon earth-abundant, readily available, and nontoxic metal centers. In this regard, we have also shown that these catalytic reactions, as applied to polyolefins, are viable to compete with conventional syntheses of fatty alcohols. The current catalytic materials deconstruct polyolefins through a process that favors the cleavage of long chains. In this scenario, the cleavage of longer chains has a more dramatic effect on the observed average molecular weight of the products than the cleavage of shorter chains. Thus, on-going efforts involve catalytic architectures, such as those that operate via processive mechanisms, which lead to narrow distributions of fatty-aluminum products. This process could motivate recovery of discarded polyolefins from the environment, produce value-added chemical products, and offer an environmentally friendly end-of-life for materials currently destined for landfills.
EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Aaron Sadow (sadow@iastate.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

The raw NMR and IR spectra, generated during this study and shown in the supplemental information, are available at Datashare, an open-access repository at Iowa State University at https://doi.org/10.25380/iastate.13626731.

Representative procedure for catalytic aluminination of polyolefins

Caution: Small organoaluminum compounds AlMe3, AlEt3, AlBu3, AlPh3 are pyrophoric and must be handled under air-free conditions. The fatty alkylaluminum products should be carefully quenched with air after full conversion of organoaluminum reagents. The HDPE reactant (1.00 g; $M_n = 6.2$ kDa, $M_w = 38.6$ kDa, $D = 6.2$), Zr(CH2CMe3)3@SiAlOx (0.13 g, 0.039 mmol Zr; see supplemental experimental procedures for synthesis and characterization), and AlBu3 (100 μL, 0.40 mmol) were loaded into a glass tube equipped with a glass-encapsulated magnetic stir bar. The tube was sealed by a stainless steel UltraTorr fitting to a closed glass tube with a sidearm containing a re-sealable Teflon-glass valve. The vessel was heated in an aluminum block at 200°C for 12 h. The volatile components of the headspace were sampled and analyzed by GC-MS, which revealed isobutylene to be the primary species. At the end of 12 h, the contents of the tube were quenched by passing dry air into the vessel for 1 h through the sidearm. The crude reaction mixture was extracted with CH2Cl2 (3 × 5 mL), and the volatile components were evaporated from the liquid to provide an oil (0.40 g, 40% based on starting HDPE mass) which was further analyzed by spectroscopic and analytical techniques (NMR, IR, GC-MS, MALDI-TOF-MS). MALDI-TOF-MS revealed a C34-centered distribution of fatty alcohols, which was corroborated by similar distributions obtained from CO2, I2, and MeOH quenched experiments. The residual solid was dissolved in hot 1,2-dichlorobenzene and filtered to remove the catalyst. A solid precipitates from the filtrate upon cooling. The supernatant liquid was decanted, and the solid polymer was washed with CH2Cl2 (3 × 5 mL), dried under vacuum, and analyzed by IR spectroscopy.

Summary of process design

A technoeconomic analysis was conducted for a conceptual plant that processes 250 MT/day of PE. The conceptual plant, at 90% utilization, produces 70,847 kg fatty alcohol sulfate per day, co-produces 27,295 kg C40 lubricant product per day, 14,222 kg AlCl3 salt per day, and 117,833 kg asphalt per day. The co-produced light hydrocarbons are combusted to generate electricity and steam for onsite use, and the surplus electricity of 122,777 kWh/day is exported for sale. By using market prices for feedstocks, reagents, catalysts, and other material input and co-products, the minimum market selling prices for C40 fatty alcohol sulfate is $3.41/kg. Given the high market value of fatty alcohols in the range of $20–60/kg (the market price of C40 fatty alcohol sulfate is not available but is expected to have much higher values than that of fatty alcohol precursors), the process is likely to be highly profitable.
SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.chempr.2021.03.007.

ACKNOWLEDGMENTS

This work was supported as part of the Institute for Cooperative Upcycling of Plastics (iCOUP), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences (BES), and Catalysis for Polymer Upcycling (CPU) funded by DOE-BES, Division of Chemical Sciences, Geosciences, and Biosciences, under contracts DE-AC-0207CH11358 (Ames Laboratory) and DE-AC-02-06CH11357 (Argonne National Laboratory).

AUTHOR CONTRIBUTIONS

Conceptualization, U.K. and A.D.S.; methodology, U.K., A.D.S., P.S., and F.A.P.; investigation, U.K., G.Z., A.L.P., and R.H.; resources, P.C. and I.I.S.; writing – original draft, U.K. and A.D.S.; writing – review & editing, U.K., A.D.S., F.A.P., P.S., and M.D.; funding acquisition, A.D.S., M.D., and F.A.P.; supervision, A.D.S., P.S., F.A.P., and M.D.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: November 18, 2020
Revised: January 28, 2021
Accepted: March 8, 2021
Published: April 9, 2021

REFERENCES

1. Kennedy, A.R., Klett, J., Mulvey, R.E., and Wright, D.S. (2009). Synergetic sedation of sensitive anions: alkali-mediated zincation of cyclic ethers and ethene. Science 326, 708–708.

2. Chen, H., Schlacht, S., Semple, T.C., and Hartwig, J.F. (2000). Thermal, catalytic, regiospecific functionalization of alkanes. Science 287, 1995–1997.

3. Cho, J.Y., Tse, M.K., Holmes, D., Maleczka, R.E., and Smith, M.R. (2002). Remarkably selective iridium catalysts for the elaboration of aromatic C-H bonds. Science 295, 305–308.

4. Pitts, C.R., Bloom, M.S., Bume, D.D., Zhang, Q.A., and Leckta, T. (2015). Unstrained C-C bond activation and directed fluorination through photocatalytically-generated radical cations. Chem. Soc. Ed. 5225–5229.

5. Roque, J.B., Kuroda, Y., Gottemann, L.T., and Sarpong, R. (2018). Deconstructive fluorination of cyclic amines by carbon-carbon cleavage. Science 361, 171–174.

6. Morcillo, S.P. (2019). Radical-promoted C–C bond cleavage: a deconstructive approach for selective functionalization. Angew. Chem. Int. Ed. 58, 14044–14054.

7. Gozin, M., Weisman, A., Ben-David, Y., and Milstein, D. (1993). Activation of a carbon–carbon bond in solution by transition-metal insertion. Nature 364, 699–701.

8. Basset, J.M., Copéret, C., Soulivan, D., Taoufiq, M., and Caaz, J.T. (2010). Metathesis of alkanes and related reactions. Acc. Chem. Res. 43, 323–334.

9. Hasch, M.C., Kus, S., Brookhart, M., and Goldman, A.S. (2012). Alkane metathesis by tandem alkane-dehydrogenation–olefin-metathesis catalysis and related chemistry. Acc. Chem. Res. 45, 947–958.

10. Flaherty, D.W., Hicklitt, D.D., and Iglesia, E. (2014). Metal-catalyzed C–C bond cleavage in alkanes: effects of methyl substitution on transition-state structures and stability. J. Am. Chem. Soc. 136, 9664–9676.

11. Flaherty, D.W., and Iglesia, E. (2013). Transition-state enthalpy and entropy effects on reactivity and selectivity in hydrogenolysis of n-alkanes. J. Am. Chem. Soc. 135, 18586–18599.

12. Lecuyer, C., Quignard, F., Choplin, A., Olivier, D., and Basset, J.M. (1991). Surface organometallic chemistry on oxides: selective catalytic low-temperature hydrogenolysis of alkanes by a highly electrophilic zirconium hydride complex supported on silica. Angew. Chem. Int. Ed. Engl. 30, 1660–1661.

13. Cormier, J., Lefebvre, F., Evans, J., Lecuyer, C., Dufaud, V., Quignard, F., et al. (1996). Catalytic cleavage of the C-H and C-C bonds of alkanes by surface organometallic chemistry: an EXAFS and IR characterisation of a Zr-H catalyst. Science 271, 966–969.

14. Brahney, J., Hallerud, M., Heim, E., Hahnenberger, M., and Sukumaran, S. (2020). Plastic rain in protected areas of the United States. Science 368, 1257–1260.

15. Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., and Law, K.L. (2015). Marine pollution: Plastic waste inputs from land into the ocean. Science 347, 768–771.

16. Lau, W.W.Y., Shiran, Y., Bailey, R.M., Cook, E., Stuchtey, M.R., Koskella, J., Velis, C.A., Godfrey, L., Boucher, J., Murphy, M.B., et al. (2020). Evaluating scenarios toward zero plastic pollution. Science 369, 1455–1461.

17. Borrelle, S.B., Ringma, J., Law, K.L., Monnahan, C.C., Lebreton, L., McGivern, A., Murphy, E., Jambeck, J., Leonard, G.H., Hileary, M.A., et al. (2020). Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. Science 369, 1515–1518.

18. Vollmer, J., Jenks, M.J.F., Roelands, M.C.P., White, R.J., van Harmelen, T., de Wild, P., van der Laan, G.P., Meier, F., Keurentjes, J.T.F., and Weckhuysen, B.M. (2020). Beyond mechanical recycling: giving new life to plastic waste. Angew. Chem. Int. Ed. Engl. 59, 15402–15423.
32. Dufaud, V., and Basset, J.M. (1998). Catalytic recycling of waste plastics for new materials production. Nat. Rev. Chem. 1, 0046.

33. Pfifer, A., and Sen, A. (1998). Chemical recycling of plastics to useful organic compounds by oxidative degradation. Angew. Chem. Int. Ed. Engl. 37, 806–810.

34. Ziegler, K., Krupp, F., and Zosel, K. (1960). Metallorganische Verbindungen. XL Synthese von Alkalimetallen aus organoaluminium-verbindungen. Justus Liebigs Ann. Chem. 629, 241–250.

35. Ziegler, K., Krupp, F., Weyer, K., and Larbig, W. (1960). Metallorganische Verbindungen. XLI Reaktionen der aluminiumtrikyle mit kohlendioxyd und schwefeldioxyd. Justus Liebigs Ann. Chem. 629, 251–256.

36. Sanders, R.E., Jr. (2012). Aluminum and aluminum alloys. In Kirk-Othmer Encyclopedia of Chemical Technology, pp. 1–64.

37. Xu, S., and Negishi, E.I. (2016). Zirconium-catalyzed asymmetric carboalumination of unactivated terminal alkynes. Acc. Chem. Res. 49, 2158–2168.

38. Camara, J.M., Petros, R.A., and Norton, J.R. (2011). Zirconium-catalyzed carboalumination of α-olefins and chain growth of aluminum alkyls: kinetics and mechanism. J. Am. Chem. Soc. 133, 5263–5273.

39. Arriola, D.J., Carnahan, E.M., Hustad, P.D., Kuhlman, R.L., and Wenzel, T.T. (2006). Catalytic production of olefin block copolymers via chain shuffling polymerization. Science 312, 714–719.

40. O’Reilly, M.E., Dutta, S., and Veige, A.S. (2016). β-alkyl elimination: fundamental principles and polyolefin applications. Chem. Rev. 116, 8105–8145.

41. Zheng, J., Lin, Y., Liu, F., Tan, H., Wang, Y., and Tang, T. (2013). Controlled chain-scission of polybutadiene by the Schwartz hydrozirconiation. Eur. J. Chem. 19, 541–548.

42. Zakharov, V.A., Duddenko, V.K., Paukohts, A.E., Karakchiev, L.G., and Yermakov, Y.I. (1977). Formation of zirconium hydrides in supported organozirconium catalysts and their role in ethylene polymerization. J. Mol. Catal. 1, 421–435.

43. Yermakov, Y.I., Ryndin, Y.A., Alexeev, O.S., Kochubey, D.I., Shmackov, V.A., and Gergert, N.I. (1989). Hydroxide complexes of titanium and zirconium attached to SiO2 as hydrogenation catalysts. J. Mol. Catal. 49, 121–132.

44. Schwartz, J., and Ward, M.D. (1980). Silica-supported zirconium hydrides as isomerization or hydrogenation catalysts for long-chain olefins. J. Mol. Catal. 8, 465–469.

45. Pasha, F.A., Benderjou-Sejerdani, A., Huang, K.-W., and Basset, J.-M. (2014). C-H and C-C activation of n-butane with zirconium hydrides supported on SBA15 containing N-donor ligands. [{(=Si=NH) – (=Si–=NH)}] (=(=Si=NH) – (=Si–=X2)ZrH] and [{(=Si=NH) – (=Si–=X2)}]=X – NH – – –]. A DFT study. Organometallics 33, 3320–3327.

46. Rataboul, F., Baudouin, A., Thieuleux, C., Veyre, L., Copéret, C., Thivolle-Cazat, J., et al. (2004). Molecular understanding of the formation of surface zirconium hydrides upon thermal treatment under hydrogen of ([=Si=O]Zr(CH2=Bu4)] by using advanced solid-state NMR techniques. J. Am. Chem. Soc. 126, 12541–12550.
another step towards the utopian single site dream? Chem. Sci. 6, 5456–5465.

59. Kermagoret, A., Kerber, R.N., Conley, M.P., Callens, E., Florian, P., Massiot, D., Coperet, C., Delbecq, F., Rozanska, X., and Sautet, P. (2013). Triisobutylaluminum: bulkier and yet more reactive towards silica surfaces than triethyl or trimethylaluminum. Dalton Trans 42, 12681–12687.

60. Thieuleux, C., Maraval, A., Veyre, L., Coperet, C., Soulivong, D., Basset, J.M., and Sunley, G.J. (2007). Homologation of propane catalyzed by oxide-supported zirconium dihydride and dialkyl complexes. Angew. Chem. Int. Ed. Engl. 46, 2288–2290.

61. Perras, F.A., Boteju, K.C., Slowing, I.I., Sadow, A.D., and Pruski, M. (2018). Direct 17O dynamic nuclear polarization of single-site heterogeneous catalysts. Chem. Commun. 54, 3472–3475.

62. Perras, F.A., Wang, Z., Kobayashi, T., Baiker, A., Huang, J., and Pruski, M. (2019). Shedding light on the atomic-scale structure of amorphous silica–alumina and its branched acid sites. Phys. Chem. Chem. Phys. 21, 19529–19537.

63. Grey, C.P., and Vega, A.J. (1995). Determination of the quadrupole coupling constant of the invisible aluminum spins in zeolite HY with 1H/27Al TRAPDOR NMR. J. Am. Chem. Soc. 117, 8232–8242.

64. Grey, C.P., and Veeman, W.S. (1992). The detection of weak heteronuclear coupling between spin 1 and spin 1/2 nuclei in MAS NMR. 14N/13C/H triple resonance experiments. Chem. Phys. Lett. 192, 379–385.

65. Adachi, M., Neder, C., Wang, X.X., Bayard, F., Dufaud, V., Lefebvre, F., et al. (2003). Surface organometallic chemistry of zirconium. Chemical reactivity of the =Si–O–ZrNp3 surface complex synthesized on dehydroxylated silica and application to the modification of mordenite. J. Mol. Cat. A: Chem. 204–205, 443–455.

66. Backström, E., Odelius, K., and Hakkarainen, M. (2019). Designed from recycled: turning polyethylene waste to covalently attached polylactide plasticizers. ACS Sustainable Chem. Eng. 7, 11004–11013.

67. Zhao, D., Wang, X., Miller, J.B., and Huber, G.W. (2003). The chemistry and kinetics of polyethylene pyrolysis: a process to produce fuels and chemicals. ChemSusChem 13, 1764–1774.

68. Bunel, E., Burger, B.J., and Bercaw, J.E. (1988). Carbon-carbon bond activation via β-alkyl elimination: Reversible branching of 1,4-pentadienes catalyzed by scandocene hydride derivatives. J. Am. Chem. Soc. 110, 976–978.

69. Watson, P.L., and Roe, D.C. (1982). β-alkyl transfer in a lanthanide model for chain termination. J. Am. Chem. Soc. 104, 6471–6473.

70. Quintanilla, E., di Lena, F., and Chen, P. (2006). Chain transfer to aluminum in MAO-activated metallocene-catalyzed polymerization reactions. Chem. Commun. (41), 4309–4311.

71. Ewart, S., Konstantinov, I., Karjala, T., Baugh, D., iii, and Munjal, S. (2020). Aluminum alkyls as highly active catalytic chain transfer agents. Macromol. React. Eng. 14, 1900047.

72. Mogstad, A.L., and Waymouth, R.M. (1992). Chain transfer to aluminum in the homogeneous cyclopolymerization of 1,5-hexadiene. Macromolecules 25, 2282–2284.

73. Baroni, A.C.M., Arruda, C.C.P., and Carvalho, D.B. (2017). Hydroalumination of alkynes and alkynes. In PATAI’s Chemistry of Functional Groups, Z. Rappoport, ed. (John Wiley & Sons), pp. 1–24.

74. Joubert, J., Delbecq, F., Thieuleux, C., Taoufik, M., Blanc, F., Coperet, C., Thivolle-Cazat, J., Basset, J.-M., and Sautet, P. (2007). Synthesis, characterization, and catalytic properties of γ-Al2O3-supported zirconium hydrides through a combined use of surface organometallic chemistry and periodic calculations. Organometallics 26, 3329–3335.

75. Waterman, R. (2013). σ-bond Metathesis: a 30-year retrospective. Organometallics 32, 7249–7263.