RESEARCH ARTICLE

Surface Protected Organozirconium Catalyzes C–H Alumination of Saturated Hydrocarbons

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Abstract: Surface grafted organozirconium-catalyzes C–H/Et–Al exchange reactions, involving saturated hydrocarbons and $AlEt_3$, to afford organoaluminum compounds and ethane. The $Zr(O^tBu)_3@SiO_2$-$Al_2O_{3\text{-}700}$ (**1**) catalyst contains monopodal ≡SiO–$Zr(O^tBu)_3$ and only a few residual silanols (<5%). Nonetheless, these silanols are the Achille's heel of **1**, providing a pathway for surface and catalyst degradation during catalysis, limiting the alkylaluminum yield and catalyst turnover. Support degradation, involving the cleavage of Si–O bonds by activated surface organometallics, is inhibited by capping silanols with –$SiMe_3$. Residual silanols in **1** react with allyltrimethylsilane, as determined by solid-state ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, and reaction stoichiometry, to form $Zr(O^tBu)_3/SiMe_3@SiO_2$-$Al_2O_{3\text{-}700}$ (**2**), which is resistant to degradation by $AlEt_3$. C–H alumination of dodecane catalyzed by **2** produces higher yields of the 1-dodecylaluminum product in comparison to **1**, and in >95% selectivity. Additionally, methane undergoes **2**-catalyzed C–H alumination, providing a route to $AlMe_3$.

Introduction

Alkylaluminums have an outsized role in large-scale chemical manufacturing via transformations of unsaturated hydrocarbons, including as activators and chain transfer agents in olefin polymerization,[1] as reactants in the oligomerization of ethylene via the Ziegler process,[2] as well as in carboaluminations or hydroaluminations of alkenes.[3] The organoaluminum products of these reactions are valuable due to their versatility and can be readily transformed into alcohols, carboxylic acids, or organohalides, or can be used in cross-coupling, addition reactions, or olefin polymerization. In contrast to well-developed C–H borylation chemistry,[4-6] catalytic C–H alumination is limited to palladium-catalyzed reactions of diketiminate-supported aluminum(I) or dihydride reagents with arenes that gives arylaluminum products.[7, 8] The direct C–H alumination of saturated hydrocarbons could be a valuable approach in commodity-scale syntheses where inexpensive and abundant organoaluminum reactants would be advantageous. Triethylaluminum is a particularly appealing reactant for this type of process because it is prepared with atom-economy directly from ethylene, hydrogen, and aluminum, the most abundant metal in the earth's crust.[9] The byproduct of C–H alumination using $AlEt_3$ is ethane, which can be cracked into ethylene and hydrogen, and could be reused to make more $AlEt_3$ in an atom-efficient, cyclical process. Unlike exothermic oxidative C–H functionalization processes where oxidized products are often more reactive than alkanes themselves,[10] alkyl group exchange at aluminum is nearly thermoneutral, and products are less likely to undergo secondary functionalization steps.

Our choice of zirconium as the active metal site for a first-generation C–H alumination catalyst was based upon its pre-eminent role in existing aluminum-carbon bond forming processes such as carboalumination and the high reactivity of electrophilic early organo-transition metal compounds in C–H bond activation of aliphatic and aromatic hydrocarbons via σ-bond metathesis.[11-14] C–H bond cleavage via σ-bond metathesis has been proposed as the key step in a few catalytic processes, including hydrocarbon hydrogenolysis,[15-18] propane homologation,[19] dehydrogenative silylation,[20-22] hydroarylation,[23-25] and dehydrogenative borylation.[26-30] In

addition, air-stable zirconium precatalysts are activated for olefin polymerization by alkylaluminum compounds,[31] and we had found that an air-exposed, deactivated neopentoxyzirconium species could be re-activated for catalytic deconstruction of polyolefins in the presence of Al^{i}Bu$_3$.[32] These ideas led us to the first example of this C–H/Et–Al exchange approach to the C–H alumination of aliphatic hydrocarbons (eq [1]),[33] which used an air-stable, surface-supported alkoxyzirconium complex Zr(O^{t}Bu)$_3$@SiO$_2$-Al$_2$O$_{3\text{-}700}$ (**1**) as a precursor for in situ generation of the active organometallic catalyst.

$$\text{R–H} + \text{AlEt}_3 \xrightarrow{\text{cat. Zr(O}t\text{Bu)}_3\text{@SiO}_2\text{-Al}_2\text{O}_{3\text{-}700}} \text{R–AlEt}_2 + \text{Et–H} \qquad [1]$$

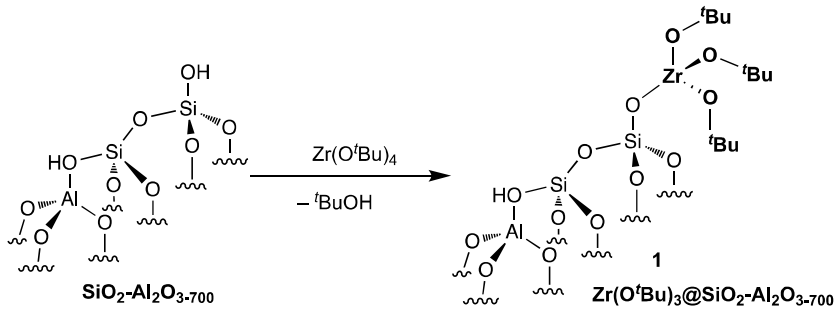
The surface organometallic chemistry (SOMC) active catalyst likely benefits from the high reactivity of surface-supported organozirconium species in C–H activations of hydrocarbons, including methane.[34, 35] SOMC catalysts on silica-alumina have been reported to be even more active than their silica-supported counterparts.[18, 19, 36] Silica-alumina was also superior as a support compared to silica in zirconium-catalyzed hydrocarbon alumination, possibly because it appeared to be less susceptible to AlEt$_3$-mediated degradation.[33] Even so, C–H alumination reactions using silica- and silica-alumina-supported systems led to the extrusion of soluble ethylsilyl species and the partial dissolution of the support material. These side reactions undoubtedly involve ethylaluminum species attacking silicon-oxygen bonds. We sought to identify the mechanisms of this attack that leads to the surface degradation and to prevent this side reaction. Not only would that immediately improve the selectivity of C–H alumination catalysis, insight from these experiments would also help establish a relationship between chemistry occurring on the support and the activity of the catalytic site.

Our approach is inspired by the silylation of metal oxides to allow catalysis in aqueous media, where dissolution of the support can be an issue. For example, reaction of zeolites with trialkylchlorosilanes prevents hydrolytic deactivation in hydrothermal catalytic reactions.[37] Likewise, the partial silylation of hydroxy groups of silica-supported titanium or tantalum catalysts improves yields of epoxidations using H_2O_2 in water.[38, 39] In addition to limiting silica hydrolysis in the latter case, increased catalytic activity is attributed to the formation of M–OSiMe$_3$ moieties. We sought to avoid such reactions at the zirconium pre-catalyst center, since the alkoxide group affected catalytic activity.[33] In addition, the oxophilicity of aluminum, its nucleophilic alkyl groups, and the non-polar environment of C–H alumination catalysis are expected to create distinct challenges compared to the established aqueous chemistry. In this vein, the high reactivity of strong Brønsted acid sites with Si$_2$Me$_6$ has been leveraged to selectively silylate sulfated zirconia in the presence of grafted ruthenium hydrosilylation catalysts.[40] Capping of Brønsted acidic sites as in SiO$_2$-Al$_2$O$_3$ or sulfated zirconia,[41] however, is not guaranteed to eliminate side reactions. Also, silylation of surface silanols with Me$_3$SiBr, prior to introduction of Cl$_2$(PCy$_3$)$_2$Ru(=CHPh), allowed coordination of Grubbs catalyst to silica-immobilized *N*-heterocyclic carbenes.[42, 43] Because we found that chloride or amide zirconium precatalysts were less active for C–H alumination than tert-butoxyzirconium, halide- and amine-free silylating agents were pursued. Here, we employ H$_2$C=CHCH$_2$SiMe$_3$[44] as a reagent for the selective silylation of residual surface hydroxy groups in **1**, to minimize the degradation of the catalyst support. That has, in turn, enabled systematic studies that led to increased catalytic turnovers, higher yields, and near-perfect selectivity for alkylaluminum products.

Results and Discussion

AlEt$_3$ Deactivates Zr(O^{t}Bu)$_3$@SiO$_2$-Al$_2$O$_{3\text{-}700}$.

We briefly describe the unprotected supported organozirconium material's composition, structure, and alumination catalysis, with respect to residual silanols and for comparison to the silylated analogues. The reaction of Zr(O^{t}Bu)$_4$ in pentane and SiO$_2$/Al$_2$O$_3$ partially dehydroxylated at 700 °C (0.66 ± 0.02 mmol OH·g^{-1}) affords **1** and ^{t}BuOH, as previously reported (eq [2]).[33]



[2]

The 0.59 ± 0.05 mmol ^{t}BuOH·g^{-1} formed in this grafting reaction and the 0.63 ± 0.03 mmol Zr·g^{-1} in **1**, measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES), nearly matched the accessible OH loading of the initial SiO_2-$Al_2O_{3\text{-}700}$ material and supported the formulation of surface species as ≡SiO–Zr(O^{t}Bu)$_3$. Quantification of the basic ligands in **1** by formic acid protonolysis as ~1.77 mmol O^{t}Bu·g^{-1} further indicated, along with the Zr loading, that there were 2.9 ± 0.2 O^{t}Bu groups per Zr center. The DNP-enhanced ^{13}C CPMAS NMR spectrum of **1** (Figure 1) contained signals at 75 ppm and 33 ppm assigned to ZrO*C*Me$_3$ and ZrOC*Me*$_3$, respectively.[45] The ν_{CH} bands in the infrared spectrum of **1**, measured in DRIFTS configuration, provided evidence for the presence of CMe$_3$ groups. The typical sharp band at 3748 cm^{-1} assigned to isolated silanols ($\nu_{SiO\text{-}H}$) in the spectrum of partially dehydroxylated SiO_2-$Al_2O_{3\text{-}700}$, however, was not detected in the IR spectrum of **1**. Instead, a broad signal at 3600 cm^{-1} indicates that surface OH species hydrogen bond, with tert-butoxyzirconium species or a restructured SiO_2-Al_2O_3 surface.

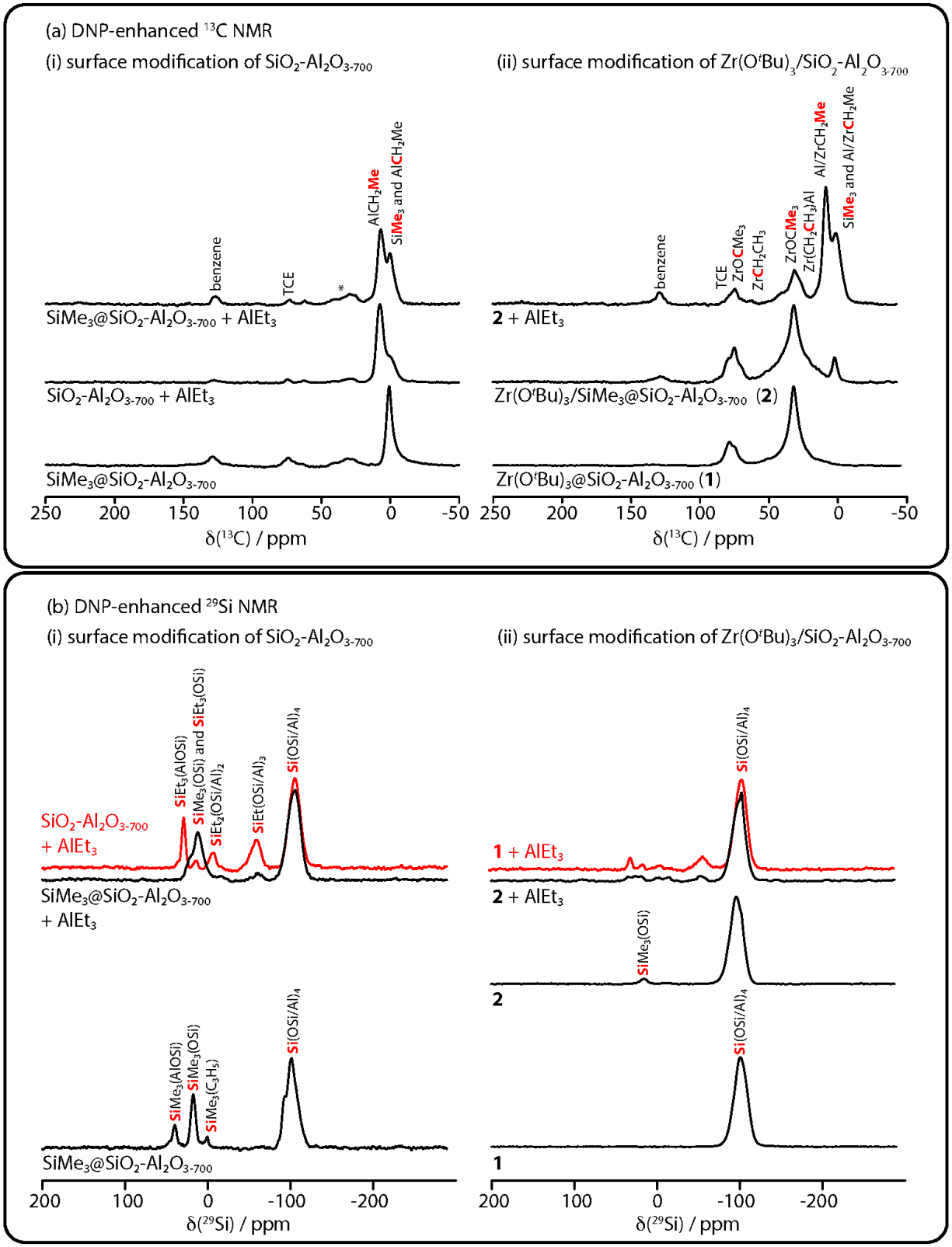


Figure 1. DNP-enhanced ^{13}C (a) and ^{29}Si (b) CPMAS NMR spectra measured for SiO_2-$Al_2O_{3\text{-}700}$ (i) and $Zr(O^tBu)_3SiO_2$-$Al_2O_{3\text{-}700}$ materials treated with 60 equiv of $AlEt_3$ and/or allyltrimethylsilane, as indicated. In (a) an asterisk denoted the presence of aliphatic impurities. SiO_2-$Al_2O_{3\text{-}700}$ and $AlEt_3$ or $SiMe_3@SiO_2$-$Al_2O_{3\text{-}700}$ and $AlEt_3$ were heated at 150 °C in dodecane prior to analysis.

We previously reported that **1** is active for the catalytic C–H alumination of *n*-dodecane.[33] For example, heating **1** (0.019 mmol Zr), $AlEt_3$ (0.57 mmol), and *n*-dodecane (1.32 mmol) gives 15 turnovers to *n*-dodecan-1-ol (0.289 mmol, 51% with respect to limiting $AlEt_3$, 22% yield with respect to n-dodecane) after workup. Reaction workup by quenching with O_2 at 0 °C followed by hydrolysis under basic conditions affords *n*-dodecan-1-ol as the only product, while acidic conditions give isomerization to secondary alcohols.

Because $AlEt_3$ is the limiting reagent under these conditions, more $AlEt_3$ could lead to higher turnovers and higher yield with respect to dodecane (Figure 2). That idea is only partly supported by the experiments. As the $AlEt_3$ is increased from 0.57 mmol (30 equiv with respect to Zr) to 1.14 mmol (60 equiv with respect to Zr), the yield of dodecan-1-ol increases to 0.367 mmol (32% with respect to limiting $AlEt_3$, 28% with respect to n-dodecane, 19 turnovers). Additional $AlEt_3$ in these experiments, unfortunately, results in poorer yields and fewer turnovers, with 150 equiv providing only 2 turnovers. Thus, for catalyst **1**, 60 equiv of $AlEt_3$ gives the highest yield of dodecan-1-ol. At the same time, the formation of soluble ethylsilyl species (~0.41 mmol ethyl·g^{-1} from 60 equiv of $AlEt_3$, determined from integrated ^1H NMR signals relative to a standard of known concentration) is increased with higher concentrations of $AlEt_3$. Thus, the effect of $AlEt_3$ on dodecylaluminum and ethylsilane yields follow opposite trends with **1** as the catalyst, suggesting that support degradation could be limiting the catalytic conversion.

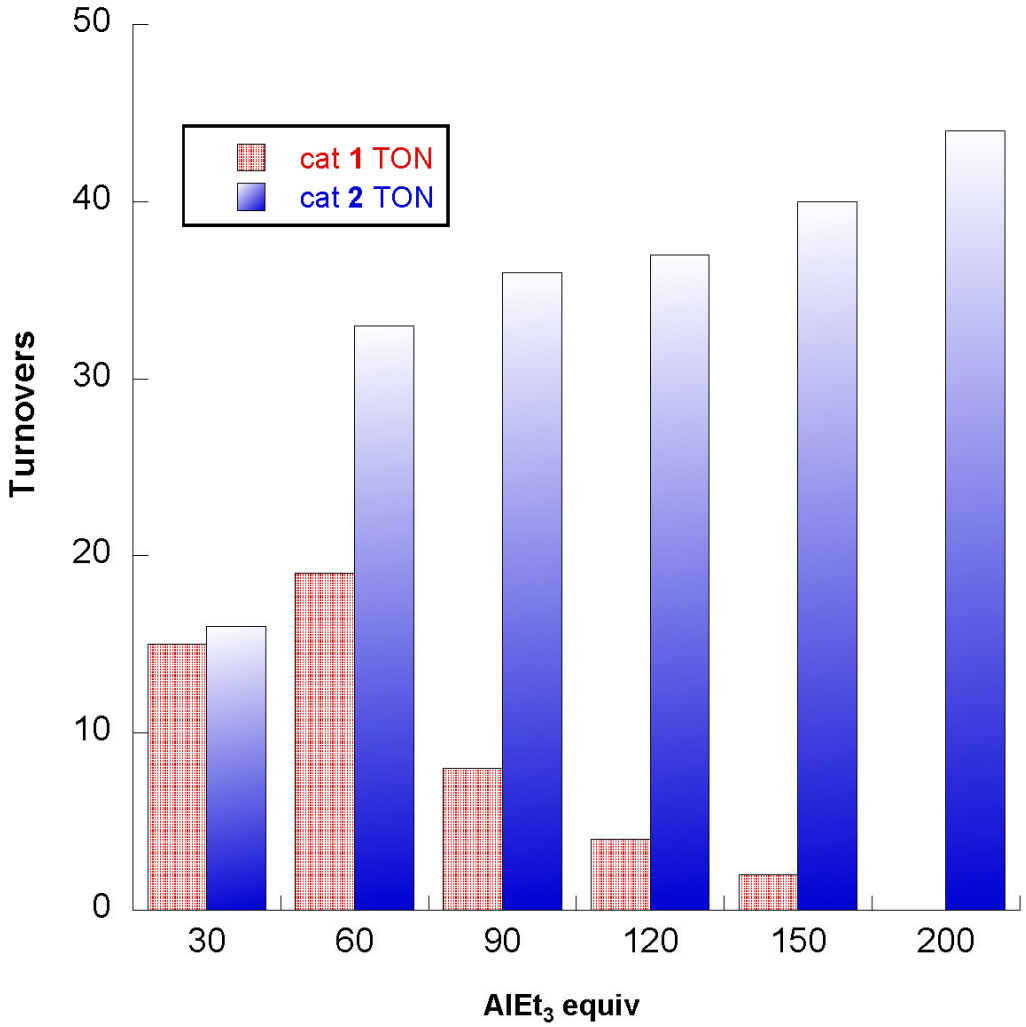


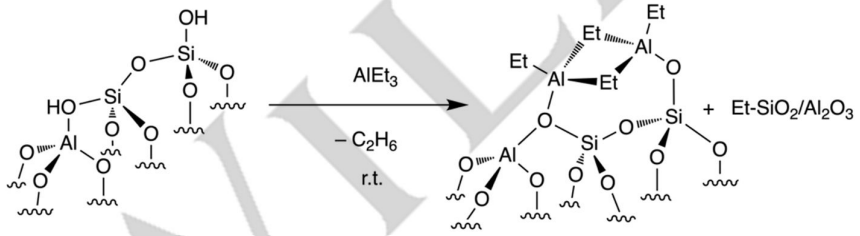
Figure 2. Decrease or increase in turnovers for dodecylaluminum formation with increasing $AlEt_3$ equivalents using catalysts **1** (red patterned bars) or **2** (blue filled bars), respectively.

After catalysis, the solid material turned dark brown, and the Al loading increased to 0.48 mmol·g^{-1} from 0.44 mmol·g^{-1} in **1**. Zr loading (0.61 mmol·g^{-1}) in the dark brown material matched that in **1**. In addition, ethylsilyl groups (≡SiEt, =SiEt$_2$, –SiEt$_3$) were observed on the surface of SiO_2-Al_2O_3 by DNP-enhanced ^{29}Si and ^{13}C CPMAS NMR spectroscopy (Figure 1). We did not detect dodecan-1-ol after workup using the dark-brown material as a recycled catalyst, in experiments performed by decanting the liquids from a first experiment and adding fresh n-dodecane and AlEt$_3$ (60 equiv with respect to Zr) to the brown solid material. Rather than give higher yields of dodecylaluminum, adding more AlEt$_3$ appears to accelerate ethylsilyl formation.

The effects of AlEt$_3$ on catalytic activity could be related to its reactions at the zirconium sites or at residual silanols on the support. **1**$^{80\%}$ was synthesized, with Zr(O^{t}Bu)$_4$ grafted at only ~80% of the OHs, to investigate how decreased Zr or increased OH loadings affect the catalysis. The Zr loading in **1**$^{80\%}$ was 0.46 ± 0.02 mmol·g^{-1} by ICP-OES, corresponding to 80% of the original protic sites in SiO_2-$Al_2O_{3\text{-}700}$ and 75% of the Zr loading of **1**. Excess MgBn$_2$ was protonated by the residual protic sites in **1**$^{80\%}$ to generate toluene, which was quantified to determine the hydroxy loading of 0.114 mmol OH·g^{-1} (i.e., ~20% of protic sites in the original SiO_2-$Al_2O_{3\text{-}700}$). The DRIFTS of **1**$^{80\%}$ contained a broad signal at 3598 cm^{-1} assigned to hydrogen-bonded silanols or bridging ≡Si(≡Al)OH,[46] while the peak assigned to isolated silanols was not observed. Under comparable conditions using equivalent mol % zirconium, *n*-dodecane (1.32 mmol), and AlEt$_3$ (30 or 60 equiv), precatalyst **1**$^{80\%}$ was much less active than **1** and yielded only 11% or 2% dodecan-1-ol (8 or 1.4 turnovers), respectively. In addition, much more ethylsilyl species (2.7 mmol EtSi·g^{-1}) were detected in the ^{1}H NMR spectrum of the deep brown reaction mixture using **1**$^{80\%}$ than in reactions catalyzed by **1**. Thus, the presence of accessible protic sites in **1**$^{80\%}$ leads to greater catalyst deactivation by AlEt$_3$ than **1** itself.

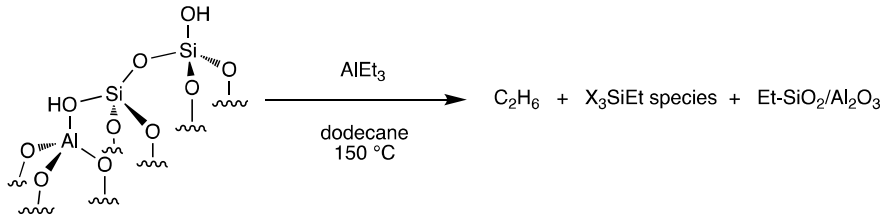
Reaction of AlEt$_3$ with SiO_2-Al_2O_3 and Surface-protected SiO_2-Al_2O_3.

Because silanols appeared to be involved in the deactivation of **1** under catalytic conditions, we investigated the degradation of SiO_2-$Al_2O_{3\text{-}700}$ itself by AlEt$_3$, in the absence of grafted zirconium species, to develop strategies to improve catalytic turnovers and product yields. The reaction of excess AlEt$_3$ (30 equiv) and partially dehydroxylated SiO_2-$Al_2O_{3\text{-}700}$ (20 mg; 0.66 ± 0.02 mmol OH·g^{-1} measured by reaction with MgBn$_2$) at room temperature generates 0.66 ± 0.02 mmol ethane·g^{-1} (GC-FID). The ca. 0.66 mmol AlEt$_3$·g^{-1} consumed in this reaction, estimated by integration of residual ethyl signals in the ^{1}H NMR spectrum of the reaction mixture, was consistent with quantitative reaction of the –OH groups. Although the structures of the supported Al species were not determined in this work, it is reasonable to assume that they adopt similar configurations as seen on silica (eq [3]). For instance, (≡SiO)$_2$-Al$_2$Et$_4$ sites are formed on SiO_2 dehydroxylated under vacuum at 500 °C.[47]



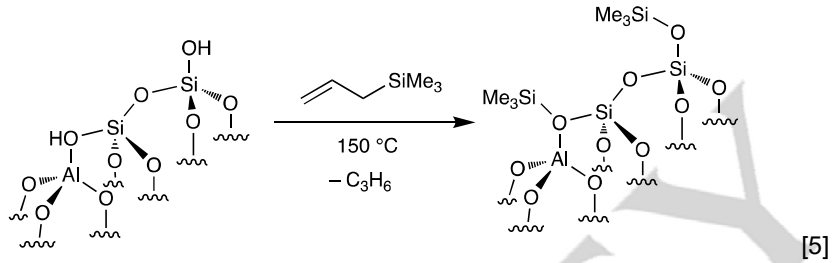
[3]

Ethylsilyl species were not detected in solution by ^{1}H NMR spectroscopy from these room temperature reaction conditions. Heating a mixture of SiO_2-$Al_2O_{3\text{-}700}$ (40 mg) and AlEt$_3$ (1.26 mmol) in *n*-dodecane at 150 °C for 12 h (eq [4]; conditions typically used for catalytic C–H alumination) forms, in addition to ethane, soluble species with ethylsilyl groups (1.20 mmol·g^{-1}) corresponding to ~2× the initial silanols present in SiO_2-$Al_2O_{3\text{-}700}$ and equivalently 2× the amount of AlEt$_3$ that was grafted onto the surface at room temperature. ^{29}Si dynamic nuclear polarization (DNP)-enhanced cross polarization magic-angle spinning (CPMAS) NMR of SiO_2-$Al_2O_{3\text{-}700}$ heated with AlEt$_3$ at 150 °C shows that Et$_3$Si(OSi/Al) (23 and 8 ppm), Et$_2$Si(OSi/Al)$_2$ (-13 ppm), and EtSi(OSi/Al)$_3$ (-66 ppm) surface sites formed (see Figure 1). Similar ^{29}Si NMR signals were observed in SiO_2-Al_2O_3 samples that were allowed to react with AlEt$_3$ at only room temperature. Thus, silicon has been alkylated by its reaction with AlEt$_3$.



[4]

The degradation of silica-alumina under these conditions could involve either the direct alkylation of surface siloxanes by $AlEt_3$ from solution, covalently grafted ethylaluminum species attacking nearby surface siloxanes, or grafted ethylaluminum sites mediating the reaction of solution-phase $AlEt_3$ and siloxanes. The first possible pathway was tested by heating $AlEt_3$ with a trimethylsilyl-capped silica-alumina, which had a very low loading of surface silanols to limit the sites for $AlEt_3$ grafting. The trimethylsilyl-protected silica-alumina $Me_3Si@SiO_2$-$Al_2O_{3\text{-}700}$ itself was prepared by treatment of SiO_2-$Al_2O_{3\text{-}700}$ with $H_2C{=}CHCH_2SiMe_3$ at 150 °C in pentane in a sealed pressure vessel (eq [5]).[44] This capping reaction evolved 0.65 ± 0.03 mmol propylene $\cdot g^{-1}$, corresponding to quantitative consumption of the accessible surface silanols. The quantitative capping of surface silanols was also supported by reaction of $Me_3Si@SiO_2$-$Al_2O_{3\text{-}700}$ with $MgBn_2$, which revealed that only ~0.004 mmol $OH\cdot g^{-1}$ remained in the material.



[5]

DNP-enhanced ^{29}Si CPMAS NMR measurements of $Me_3Si@SiO_2$-$Al_2O_{3\text{-}700}$ (Figure 1) revealed surface ≡SiO–$SiMe_3$ (18 ppm) and bridging ≡Si(≡Al)O–$SiMe_3$ (41 ppm) sites, with the latter being shifted due to the more polar bonding to the support.[48] Semi-quantitative integration of these sites suggests that ca. 1/3 of the surface hydroxys are of the bridging variety. This ratio agrees reasonably well with the 27% Al loading of the SiO_2-Al_2O_3. The surface $SiMe_3$ groups are also evident by DNP-enhanced ^{13}C CPMAS NMR at 2 ppm.

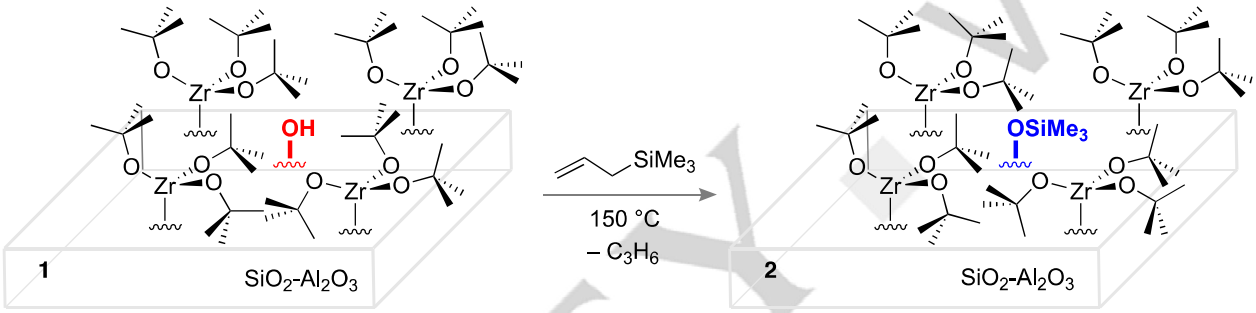
The reaction of $Me_3Si@SiO_2$-$Al_2O_{3\text{-}700}$ with excess $AlEt_3$ (30 equiv) at room temperature evolved only ~0.002 mmol ethane$\cdot g^{-1}$. The ^{13}C and ^{29}Si SSNMR spectra of the $AlEt_3$-treated $Me_3Si@SiO_2$-Al_2O_3 were largely identical to $Me_3Si@SiO_2$-Al_2O_3 itself, displaying surface $SiMe_3$ in addition to a small amount of new AlEt sites. Notably, surface alkylation products were reduced by approximately one order of magnitude, as compared to that seen in unprotected SiO_2-$Al_2O_{3\text{-}700}$ (Figure 1). In further contrast to the degradation of SiO_2-$Al_2O_{3\text{-}700}$ in the presence of $AlEt_3$, soluble ethylsilyl species were not detected after reaction of excess $AlEt_3$ and $Me_3Si@SiO_2$-$Al_2O_{3\text{-}700}$ in *n*-dodecane at 150 °C for 12 h. Thus, ≡Si–O–Si≡ and ≡Si–O–$SiMe_3$ surface linkages are inert to direct alkylation by $AlEt_3$ from solution.

The second possible pathway for support degradation, in which covalently grafted ethylaluminum surface moieties extrude ethylsilyl species, was ruled out by isolating $AlEt_3$-treated SiO_2-$Al_2O_{3\text{-}700}$ and then heating that material in dodecane at 150 °C for 12 h. Under these conditions in the absence of free $AlEt_3$, soluble ethylsilyl species were not detected by GC or NMR spectroscopy. Heating the isolated $AlEt_3$-treated SiO_2-$Al_2O_{3\text{-}700}$ with free $AlEt_3$ in dodecane, however, produced soluble ethylsilyl species. Thus, surface degradation, at least in the absence of other surface organometallics, involves reaction of solution-phase $AlEt_3$ with surface-grafted organoaluminum sites. These results further show that support degradation from reaction with $AlEt_3$ does not require zirconium as a catalyst or mediator, and that capping of protic sites passivates the surface against reaction with $AlEt_3$ by blocking the grafting step. These conclusions suggest that protecting any residual ≡SiOH and ≡Si(≡Al)OH grafting sites in **1** might inhibit support degradation and increase turnover numbers in the catalytic C–H alumination.

Silanol Capping to Improve Catalytic C–H Alumination.

Because grafting of $AlEt_3$ onto SiO_2-$Al_2O_{3\text{-}700}$ is a part of a pathway for surface degradation, and experiments on zirconium-free SiO_2-$Al_2O_{3\text{-}700}$ show its reactions with $AlEt_3$ can be blocked by surface silylation, the capping of residual protic sites in **1** or $\mathbf{1}^{80\%}$ could be a strategy to improve C–H alumination catalysis. Me_3SiCl, as a typical silylating agent, slowly reacts with **1** at room temperature in benzene-d_6 to form ^{t}BuOH and ^{t}BuOSiMe$_3$ along with (presumably) chlorozirconium surface species. Note that Zr(O^{t}Bu)$_4$ itself reacts with Me_3SiCl slowly in refluxing benzene-d_6 or toluene-d_8 (~8% Zr(O^{t}Bu)$_4$ conversion after 3 h). In contrast, $H_2C{=}CHCH_2SiMe_3$ and Zr(O^{t}Bu)$_4$ return only starting materials under that condition. Thus, $H_2C{=}CHCH_2SiMe_3$ was selected as the silylating agent to avoid side reactions of the ≡SiO–Zr(O^{t}Bu)$_3$ pre-catalyst site.

The reaction of **1** (0.63 mmol Zr·g^{-1}) and $H_2C{=}CHCH_2SiMe_3$ (0.164 mmol) at 150 °C gave **ZrO^{t}Bu$_3$/SiMe$_3$@SiO$_2$-Al$_2$O$_{3\text{-}700}$** (**2**; Scheme 1) and generated propylene (0.07 ± 0.03 mmol·g^{-1}, quantified by GC), which matched the estimated loading of residual accessible silanols in **1** (0.04-0.07 mmol·g^{-1}). $\mathbf{1}^{80\%}$ was similarly treated with $H_2C{=}CHCH_2SiMe_3$ to make $\mathbf{2}^{80\%}$. DNP-enhanced ^{13}C and ^{29}Si CPMAS NMR spectra of **2** detect O–SiMe$_3$ as minor surface species, in agreement with the low residual concentration of silanols in **1** (Figure 1). Notably, the DRIFTS of **2** did not contain the broad, weak feature at 3600 cm^{-1} associated with the bridging silanols in **1** (Figure 3). The comparison of $\mathbf{1}^{80\%}$ and $\mathbf{2}^{80\%}$ using DRIFTS also showed the consumption of residual OHs (Figures S4, S5).



Scheme 1. Selective silylation of residual surface OH in **1** in the presence of grafted tert-butoxyzirconium species to form **2**.

In these capping experiments, we did not detect ^{t}BuOSiMe$_3$, which could have formed from an unwanted reaction of ZrO^{t}Bu moieties and $H_2C{=}CHCH_2SiMe_3$. The Zr loading in **2** of 0.59 ± 0.03 mmol·g^{-1} was equivalent to the loading of Zr in **1**. In addition, reaction of **2** with formic acid released 1.65 mmol of ^{t}BuOH·g^{-1}, corresponding to 2.8 O^{t}Bu per Zr, within error of expectation. The Zr loading in the $\mathbf{2}^{80\%}$ material was 0.44 ± 0.02 mmol·g^{-1}. Thus, the pre-catalyst sites are equivalent in **1** and **2**.

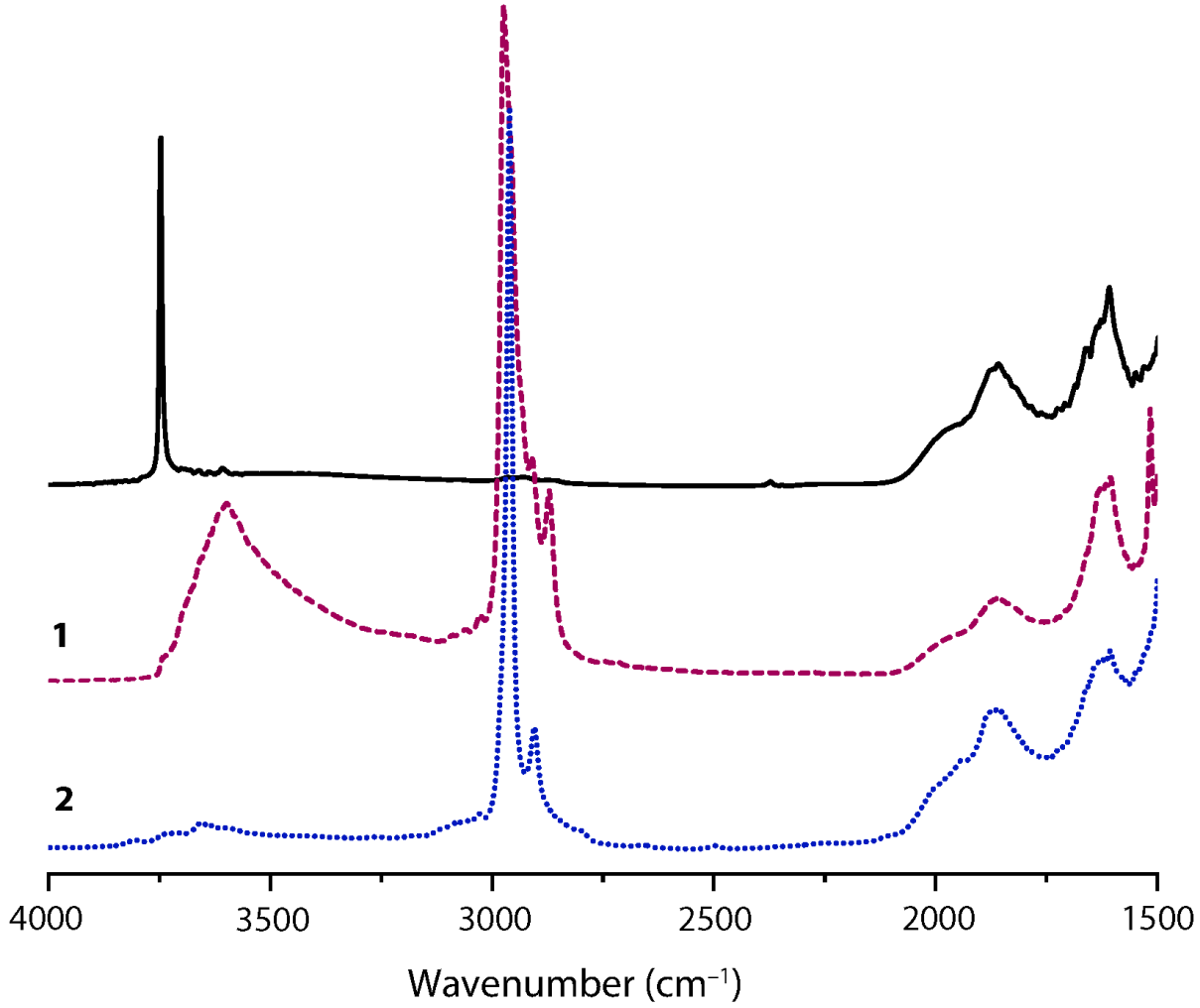
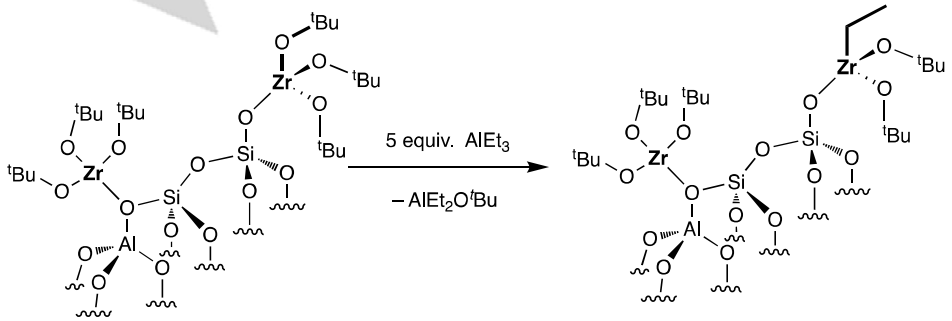


Figure 3. DRIFTS of SiO_2-$Al_2O_{3\text{-}700}$ (black continuous), **1** (grey dashed) and **2** (blue dotted), normalized to the silicon framework signal at 1610 cm^{-1}.

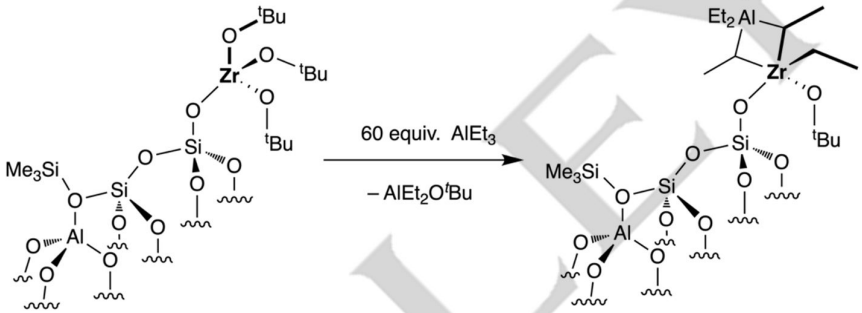
The reaction of **1** and $AlEt_3$ (5 equiv with respect to Zr) in benzene-d_6 at room temperature over 4 h forms ^{t}BuO$AlEt_2$, ethane (0.058 mmol·g^{-1}) and a deep brown solid. 18% of the total tert-butoxy (0.054 mmol·g^{-1}) in **1** transfer to soluble aluminum species, suggesting that the material contains ≡SiO–$ZrEt(O^tBu)_2$ and ≡SiO–$Zr(O^tBu)_3$ surface species in a ca. 1:1 ratio under these conditions (eq [6]).



[6]

While transfer of tert-butoxy groups is barely detectable with only 2 equiv of $AlEt_3$, the extent of exchange of tert-butoxy and ethyl groups increases with the addition of more $AlEt_3$. Reaction of 60 equiv of $AlEt_3$ and **1** gives 2 equiv of $^tBuOAlEt_2$ relative to Zr, which implies that doubly-exchanged surface species, such as ≡SiO–$ZrEt_2O^tBu$, are formed (see below). Although the analysis cannot rule out mixtures also containing ≡SiO–$ZrEt(O^tBu)_2$ and ≡SiO–$ZrEt_3$ in a 1:1 ratio, and the (formally) dialkylated zirconium species is more likely because of the large excess of $AlEt_3$. Ethane is formed as a product of the protonation of $AlEt_3$ with the residual –OH groups in **1**, as in the reaction of $AlEt_3$ and SiO_2-$Al_2O_{3\text{-}700}$ above. The ethane yield (0.06 or 0.08 mmol/g) from reaction of **1** with 5 or 60 equiv of $AlEt_3$, respectively, equals the estimated silanols in **1** (0.07 mmol/g). ICP-OES of **1** treated with 5 or 60 equiv of $AlEt_3$ at room temperature revealed increased Al loading (0.37 ± 0.04 or 0.39 ± 0.03 mmol·g^{-1}, respectively) compared to SiO_2-$Al_2O_{3\text{-}700}$ (0.31 ± 0.02 mmol·g^{-1}) and **1** (0.29 ± 0.04 mmol·g^{-1}). The Zr loading of 0.58 ± 0.03 or 0.57 ± 0.03 mmol·g^{-1} after treatment with 5 or 60 equiv of $AlEt_3$ was comparable to **1** itself, suggesting that Zr is not leached from the surface by the alkylaluminum.

Reactions of **2** with 5-200 equivalents of $AlEt_3$ with respect to Zr also form *tert*-butoxyethylaluminum species in similar yields as in reactions of **1** above, implying similar ethylated zirconium species. The comparison of **1** and **2** in their reactions with 5 equiv of $AlEt_3$ showed similar $^tBuOAlEt_2$ formation, yet **2** turned light yellow and produced only 0.008 mmol EtH·g^{-1}, approximately one order of magnitude less than from the corresponding reaction of **1** (0.058 mmol·g^{-1}). Increases in $AlEt_3$ (i.e., at 60, 150, or 200 equiv of $AlEt_3$ with respect to Zr) also transferred ~66% of the tert-butoxy groups from **2** to Al, produced 0.034 mmol EtH·g^{-1}, and afforded a yellow material. The surface species ≡SiO–$ZrEt_2O^tBu$ in this material are suggested by the reaction stoichiometry, however, these are likely $AlEt_3$ aluminum adducts such as ≡SiO–$ZrEt(Et_2AlEt_2)O^tBu$ (eq [7]) as a result of the large excess of $AlEt_3$ and possibility that $[Zr]Et_2$ would react by β-alkyl abstraction. These tentative assignments are supported by ^{13}C SSNMR signals at 55 ppm ($ZrCH_2CH_3$) and a shoulder at 20 ppm ($ZrCH_2CH_3$ and $ZrCH_2(CH_3)Al$), while the signal from $ZrCH_2(CH_3)Al$ would overlap with $AlCH_2CH_3$ at 9 ppm (Figure 1), based on comparisons to Cp_2HfEt_2 and $[Cp_2HfEt_2AlEt_2][B(C_6F_5)_4]$.[49]



[7]

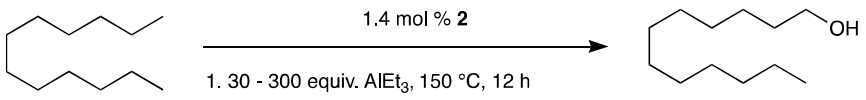
ICP-OES of **2** treated with 60 equiv of $AlEt_3$ at room temperature revealed comparable Al loading (0.31 ± 0.04 mol·g^{-1}, respectively) as SiO_2-$Al_2O_{3\text{-}700}$ (0.31 ± 0.02 mmol·g^{-1}) and **2** (0.29 ± 0.03 mmol·g^{-1}). The Zr loading of 0.57 ± 0.04 mmol·g^{-1} after treatment with 60 equiv of $AlEt_3$ was comparable to **2** itself, further suggesting that Zr is also not leached from the surface by the alkylaluminum treatments of **2** (as in **1**). Comparison of **1** and **2** treated with 60 equiv of $AlEt_3$ using DNP-enhanced ^{29}Si CPMAS NMR revealed less surface alkylation in the reaction of the latter material, and significantly less than seen with the base support (Figure 1). Based on the above results, **2** was studied as a catalyst for dodecane alumination.

Catalytic C–H Alumination of *n*-Dodecane by 2

The yield and turnovers for dodecan-1-ol formation increases with increasing $AlEt_3$ (Figure 2, blue bars), in contrast to the deactivation of **1** at high $AlEt_3$. In the reaction employing 30 equiv of $AlEt_3$ (with respect to Zr), catalyst **2** affords a slightly higher yield of dodecan-1-ol (0.308 mmol, 16 turnovers) than catalyst **1** (0.289 mmol, 15 turnovers). Doubling $AlEt_3$ to 60 equiv with catalyst **2** affords 0.621 mmol of dodecan-1-ol, essentially doubling the turnovers to 33 and yield to 47% (with respect to dodecane). With catalyst **1**, doubling $AlEt_3$ from 30 to 60 equiv increases the turnovers from 15 to only 19. Experiments decreasing the loading of **2** with respect to dodecane, rather than increasing the equivalents of $AlEt_3$, gives lower yields. Thus, reactions using 0.5 mol % Zr, compared to the 1.4 mol % catalyst in the above experiments, provides only 10.1% yield of dodecan-1-ol (corresponding to 19 turnovers). Moreover, $\mathbf{2}^{\mathbf{80\%}}$ gave comparable results as **2** under similar conditions. For instance, 0.019 mmol of Zr (in material $\mathbf{2}^{\mathbf{80\%}}$) and 60 equiv of $AlEt_3$ (with respect to Zr), gave 48% (0.636 mmol)

conversion of dodecane and 46% yield (0.611 mmol) of dodecan-1-ol, corresponding to 32 turnovers and 96.1% selectivity. Still, lower mol % Zr with **2**, or lower loading of Zr in $\mathbf{2}^{80\%}$, followed the trend of increasing turnovers with increasing equivalents of $AlEt_3$ established for 1.4 mol % **2**. In contrast, uncapped $\mathbf{1}^{80\%}$ was a poor C–H alumination catalyst under these conditions, and experiments using 0.5 mol % Zr of catalyst **1** do not provide detectable dodecan-1-ol.

The turnovers and dodecan-1-ol yield in reactions catalyzed by **2** increase monotonically with increasing $AlEt_3$ in the reactor, up to a TON of 44 and 63% yield with 200 equiv of $AlEt_3$ (eq [8]). Even at this higher dodecane conversion, selectivity for the product is 97%.



[8]

Only traces of ethylsilyl species (0.008 mmol) were observed by ^{1}H NMR spectroscopy when 200 equiv of $AlEt_3$ were used, which is two orders of magnitude less than observed with **1** as catalyst. Experiments employing 300 equiv of $AlEt_3$ with respect to Zr afforded equivalent yields of dodecan-1-ol (0.839 mmol with respect to n-dodecane, TON of 44) as experiments using 200 equivalents. The yield does not increase with longer reaction times. The higher yields and turnovers with **2** provide a stark contrast to the precipitous fall of dodecan-1-ol yield and turnovers with increasing $AlEt_3$ using catalyst **1**. That is, the large excess of $AlEt_3$ does not lead to deactivation of the active catalyst from **2** (or $\mathbf{2}^{80\%}$) because yields do not decrease as they do with **1**. Thus, we conclude that $Me_3SiCH_2CH{=}CH_2$ treatment increases the lifetime of **2** compared to **1**. Nonetheless, the yield of dodecan-1-ol reaches a plateau of ~65% at the higher concentrations of $AlEt_3$.

The color of the material from **2** was pale yellow after the catalytic reaction, in contrast to the change in color of **1** to brown. Addition of a fresh portion of dodecane (1.32 mmol) and fresh $AlEt_3$ (60 equiv with respect to Zr) to the used sample of **2** yielded a small amount of dodecan-1-ol after workup (0.106 mmol, 8% yield with respect to n-dodecane, ~6 turnovers). Formation of ethyl silyl species (0.026 mmol) from recycled **2** greatly increased compared to that from the fresh catalyst. Although there was a clear degradation of the catalytic material after the first alumination experiment, addition of more **2** to the reaction mixture containing excess $AlEt_3$ or transfer of the reaction solution to a fresh portion of **2** (preactivated with $AlEt_3$) also did not lead to higher yield of dodecan-1-ol (after workup). Because high $AlEt_3$ did not appear to inhibit catalysis, this result suggested that dodecyldiethylaluminum was inhibiting the C–H alumination.

Yields should improve under diluted conditions if the product is competing for coordination to the active sites. Initial attempts using toluene or toluene-d_8 as a solvent did not provide the dodecan-1-ol product (or benzyl alcohol or phenol products), and dodecane was recovered from the experiment. Because **1** was previously observed to react with a large kinetic isotope effect,[33] such that dodecane-d_{26} did not react under alumination conditions, the deuterated aliphatic hydrocarbon was used as the solvent to dilute the dodecane. As with **1**, **2** did not provide detectable alumination of dodecane-d_{26}, and a 1:1 mixture of dodecane and dodecane-d_{26} gave only linear 1-$C_{12}H_{25}OH$. Neither dodecan-1-ol-d_{25} nor any isotopologues of dodecane or dodecan-1-ol ($C_{12}H_xD_{26-x}$ or $C_{12}H_xD_{25-x}OH$) were detected by GC-MS or ^{2}H-NMR spectroscopy after workup, ruling out any H/D exchange, thereby suggesting that no C–D bonds are cleaved in the catalytic transformation. These observations indicate that a very large isotope effect governs the activation of C–H bonds in this system.

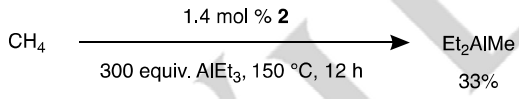
We then applied dodecane-d_{26} as a diluent to study catalytic C–H alumination of dodecane. A 1:1 mixture of dodecane (0.66 mmol) and dodecane-d_{26} (0.66 mmol) was subjected to 120 equiv $AlEt_3$ in the presence of **2** at 150 °C for 12 h. The catalysis resulted in the conversion of $C_{12}H_{26}$ to linear dodecan-1-ol (72% yield with respect to $C_{12}H_{26}$, 25 turnovers) as the primary product. The turnovers decreased compared to standard conditions, limited in part by the low initial concentration of dodecane. Therefore, a companion dilution experiment was conducted with the amount of dodecane matching standard conditions (1.32 mmol) and doubled total volume by addition of 1.32 mmol dodecane-d_{26}. Under the latter conditions, the yield and turnovers are comparable to the C–H alumination reaction of neat dodecane with 120 equiv of $AlEt_3$ and catalyst **2** (52% yield with respect to $C_{12}H_{26}$, 36 turnovers). Because dilution did not improve the turnovers, these experiments suggest that the active site is irreversibly inhibited by the reaction mixture.

We also note that dodecane-1,12-diol, the product from di-alumination and workup, was only formed in trace quantities even at relatively high conversion of dodecane. The high selectivity for mono-alumination is surprising because, by the end of the reaction, dodecyldiethylaluminum (63%) is present in higher concentration than dodecane itself (35%) and alkanes are typically less reactive than their functionalized derivatives. We considered that a functionalized product, even at that other end of the long dodecyl chain, might inhibit and/or deactivate the zirconium catalyst. To test this hypothesis, 1-trimethylsiloxydodecane ($CH_3C_{10}H_{20}CH_2$-O-$SiMe_3$) was subjected to similar catalytic conditions in the presence of the alkoxyzirconium grafted material **2** and 120 equiv of $AlEt_3$. There was no observable conversion of the substrate to HO-$CH_2C_{10}H_{20}CH_2$-O-$SiMe_3$ upon alkaline workup. To check if the catalyst was undergoing degradation or deactivation in the presence of the substrate, a 1:1 mixture of dodecane and 1-trimethylsiloxydodecane ($CH_3C_{10}H_{20}CH_2$-O-$SiMe_3$) was subjected to catalytic conversion using the catalyst **2** and 120 equiv $AlEt_3$ at 150 °C for 12 h. In this experiment, dodecan-1-ol (12% yield with respect to dodecane, 4 turnovers) was formed while 1-trimethylsiloxyldodecane was inert. Because the intramolecular inhibitory effect was much more significant for 1-trimethylsiloxyldodecane, while the dilution of diethyldodecylaluminum did not increase turnovers, we conclude that stronger association of functional groups (including arenes) with zirconium sites limit the conversion and lead to catalyst decomposition. This association also inhibits difunctionalization of aliphatic hydrocarbons under the present conditions.

Zr-catalyzed C–H Alumination of Methane.

Because **2**-catalyzed C–H alumination did not lead to difunctionalization of dodecane, even at high conversion, this catalyst system could also be effective for the mono-functionalization of methane. In addition, if the catalyst inhibition was related to build-up of dodecyldiethylaluminum, it seemed possible that diethylmethylaluminum would show less deactivation. The alumination of methane is an appealing reaction because, while $AlEt_3$ is readily synthesized from aluminum, ethylene and hydrogen in an atom-economical pathway, $AlMe_3$ preparation requires a multistep process incorporating alkali metal reduction of $AlMe_2Cl$ that generates NaCl and Al as by-products.[50] The direct synthesis of $AlMe_3$ from $AlEt_3$ and methane would be more efficient.

The supported tert-butoxyzirconium catalyst **2**, $AlEt_3$ (60 or 300 equiv), and CH_4 (725 psi) were heated to 150 °C for 12 h in a 2 mL sealed steel reactor. The reaction mixture was then analyzed by ^{1}H NMR spectroscopy using hexamethylbenzene as an internal standard. The broad ^{1}H NMR singlet close to 0 ppm can be readily assigned to the AlMe group using phase edited ^{13}C-^{1}H HSQC experiments. The turnover number increases following the trends seen for dodecane (60 equiv $AlEt_3$: 19.7% yield based on CH_4, 42 turnovers; 300 equiv $AlEt_3$: 33.4% yield based on CH_4, 71 TON, eq [9]). Thus, surface silylation doubled the turnovers and yield compared to that obtained from catalyst **1**, which gave 9% yield and 19 turnovers in an experiment using 60 equiv of $AlEt_3$. Moreover, **1** yielded negligible amounts of methylaluminum in experiments using 150 equiv of $AlEt_3$.



[9]

Conclusion

The reaction of $Zr(O^tBu)_4$ with SiO_2-$Al_2O_{3\text{-}700}$ yields **1**, containing 0.63 mmol of Zr·g^{-1} and leaving ~0.03 mmol g^{-1} of unreacted accessible –OH groups, which is less than 5% of the original hydroxy groups in the silica-alumina. We have found that these few OH groups create a pathway for catalyst decomposition in **1**-catalyzed C–H alumination of *n*-dodecane, via $AlEt_3$ grafting and subsequent attack by additional free $AlEt_3$. This pathway limits the catalytic C–H alumination with **1** because undesired ethylsilane side-products from silica ethylation increase as $AlEt_3$ concentration increases. At the same time, the yield of dodecan-1-ol decreases as $AlEt_3$ concentration increases.

A solution to the side reaction and catalyst decomposition is provided by capping the few residual silanols in **1** with $SiMe_3$ groups by reaction with $Me_3SiCH_2CH{=}CH_2$, producing **2**. **2** contains identical ≡SiO–$Zr(O^tBu)_3$ sites as in **1,** yet **2** gives more turnovers and is more selective for the catalytic C–H alumination of dodecane. In the presence of **2**, dodecan-1-ol is formed in up to 72% yield while the formation of unwanted ethylsilanes is suppressed. The surface silylation in **2**, and the resistance of **2** toward $AlEt_3$-mediated degradation, is supported by solid-state ^{13}C and ^{29}Si NMR experiments comparing **1** and **2** before and after $AlEt_3$ treatment.

Unlike **1**, catalyst **2** is not deactivated by high $AlEt_3$ concentrations; however, yields are apparently limited by the dodecyldiethylaluminum product, as evidenced by the lack of activity of fresh **2** added to reaction mixtures of $C_{12}H_{25}AlEt_2$ and $AlEt_3$, the higher yields when the reaction mixture is diluted with dodecane-d_{26}, and the higher turnovers obtained with methane than dodecane. Likely, the differing reactivity of dodecyldiethylaluminum, triethylaluminum, and diethylmethylaluminum is related to the stability of their dimers $(C_{12}H_{25}AlEt_2)_2$, $(AlEt_3)_2$, and $(Et_2AlMe)_2$, where the bridging methyl group in the latter limits its reactivity with the zirconium catalyst compared to $(AlEt_3)_2$ and $(C_{12}H_{25}AlEt_2)_2$. Because the resulting mixed alkyl(diethyl)aluminum species undergo rapid alkyl group exchange, the lowest-boiling trialkylaluminum species can be purified by distillation (e.g., Me_3Al), and the residual $AlEt_3$ can be recovered for future use. Thus, the high selectivity of catalyst **2** for mono-functionalization at the ends of aliphatic chains provides significant opportunity for applying this catalytic alumination in commodity-scale synthesis.

Data Availability Statement

The DRIFTS and NMR spectral data and GC data generated during this study and shown in the manuscript and its Supporting Information are available at DataShare, an open-access repository at Iowa State University at https://doi.org/10.25380/iastate.29437283

Supporting Information

Experimental description of the syntheses and characterization of supported zirconium catalysts **1**, $\mathbf{1}^{80\%}$, **2**, and $\mathbf{2}^{\mathbf{80\%}}$, and results of catalytic C–H alumination studies.

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Keywords: CH activation • methane functionalization • surface organometallic chemistry • catalysis • hydrocarbon alumination

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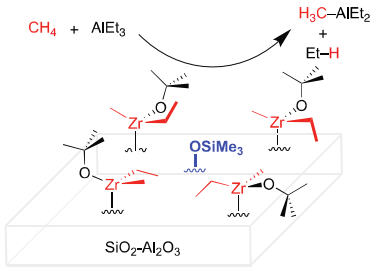
Entry for the Table of Contents

Action at organozirconium



happens when silanols are capped!

C–H alumination of saturated aliphatic hydrocarbons is catalyzed by surface-grafted organozirconium species, with high selectivity for the least-hindered, terminal position, enabled by selective silylation of a small number of residual silanols in the catalyst. Exclusive mono-alumination of methane is accomplished with more than 70 turnovers.