VIP Aluminum Hydrides

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Heteronuclear NMR Correlations To Probe the Local Structure of Catalytically Active Surface Aluminum Hydride Species on γ-Alumina**

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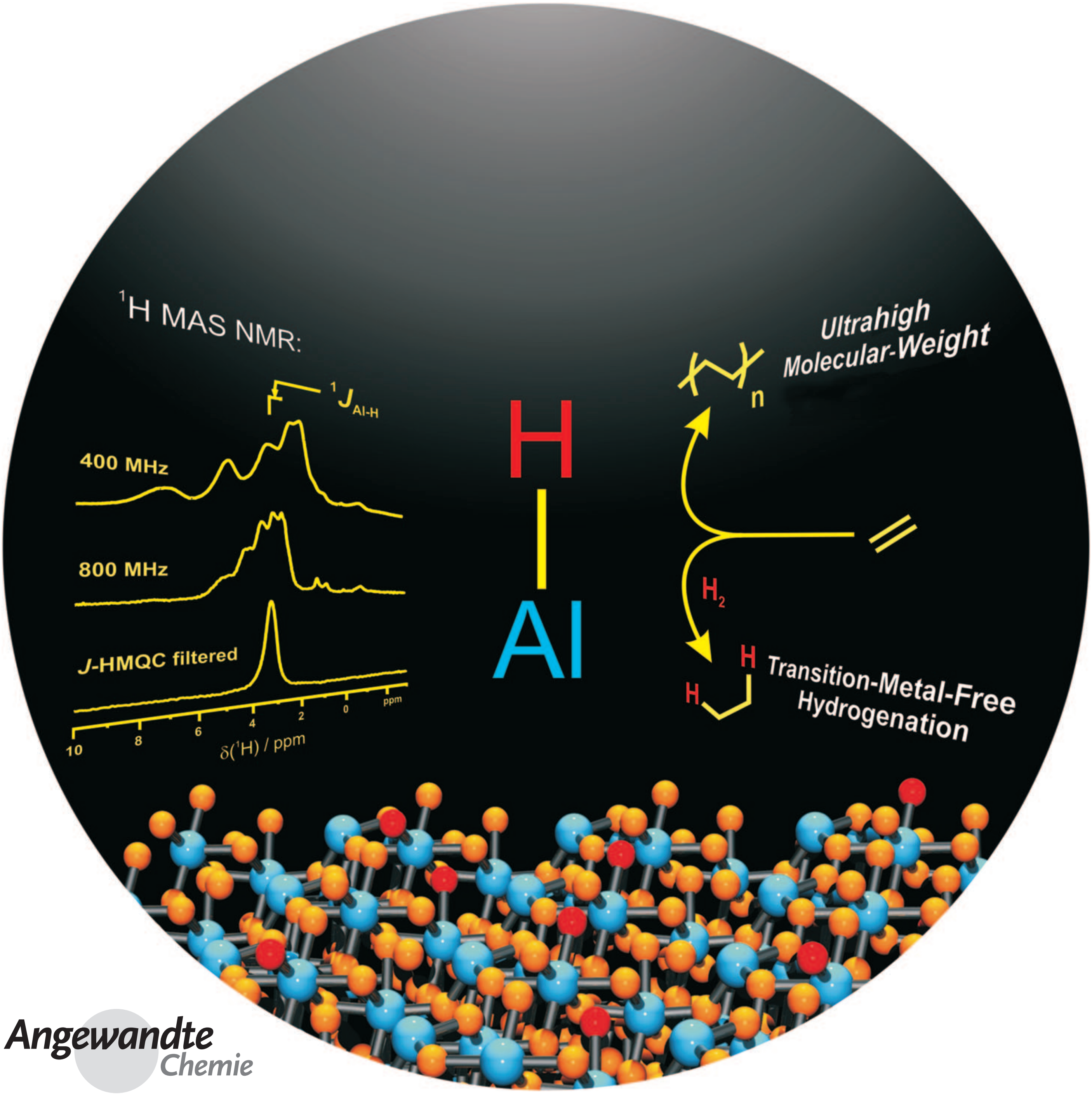

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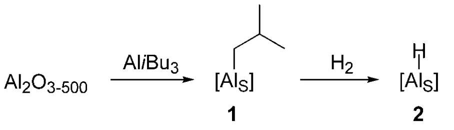
Metal hydrides are a class of species that occupy a most peculiar position on the fringes of inorganic and organometallic chemistry. Linking the lightest element of the periodic table to a wide range of transition- and main-group metals, metal hydrides have found applications in hydrogen storage,[1a] organic synthesis,[1b] and catalysis.[1c] We and others have reported on several well-defined transition-metal hydrides supported on inorganic carriers; they are active in hydrocarbon-centered reactions, such as alkane hydrogenolysis, Ziegler–Natta (de-)polymerization, and alkane and alkene metathesis, to mention only the most salient examples.[2] Supported main-group metal hydrides have been somewhat overlooked, as they are deemed to be less suitable for catalysis. However, considering recent advances in catalysis with main-group metals,[3] it seems of interest to take a closer look at this class of compounds, as they may display unforeseen reactivity.

In the course of studies on (silica-) alumina-supported catalysts, we encountered formation of surface aluminum hydrides on several occasions.[4] The chemical pathway leading to these species has only been the subject of assumptions, and their reactivity may be masked by that of the neighboring transition-metal hydrides. Therefore, it is highly desirable to efficiently and selectively synthesize surface aluminum hydrides and to characterize them with the highest possible accuracy. Supported aluminum hydrides have been studied by infrared spectroscopy,[5] but their low concentration hampers characterization by NMR spectroscopy, not only by ^{1}H but most crucially, by the less responsive ^{27}Al NMR experiments. We report here the high-yielding synthesis of supported aluminum hydrides along with their thorough characterization by high-field, multinuclear NMR spectroscopy.

In a continuation of our work on alumina-supported catalysts,[4] we selected a γ-alumina sample that had been annealed under vacuum at 500 °C (Al_2O_{3-500}), featuring a specific area of 200 m^2g^{-1}.[6] Such material bears surface hydroxyl groups, which may react with organometallic species by protonolysis, with a density of about 2.0 OH groups per nm^2 (650 $\mu mol\,g^{-1}$).[6] Furthermore, the thermal treatment creates Lewis acidic sites that are highly electrophilic and therefore, reactive towards organometallic species either during the grafting step or in a consecutive pseudo-intramolecular step in which grafted species react with neighboring surface-reactive centers by alkyl-group transfer.[7] This dual-reactivity pattern stemming from alumina's complex structure, coupled to the fact that both the incoming reagent and the inorganic carrier are based on the same element (Al), makes the present study most challenging, since we are attempting to understand molecular processes at hand and the structure of the formed surface species.

Al_2O_{3-500} reacts smoothly at room temperature with a pentane solution of $Al(i\mathrm{Bu})_3$ ($i\mathrm{Bu} = CH_2CH(CH_3)_2$) to afford a surface-modified alumina bearing Al*i*Bu moieties [**1**, Eq. (1)].



$$Al_2O_{3-500} \xrightarrow{Al i\mathrm{Bu}_3} [Al_S] \xrightarrow{H_2} \overset{H}{[Al_S]} \quad (1)$$

1 2

The infrared spectrum of **1** is almost devoid of bands in the $\nu_{(AlO-H)}$ region (Figure 1): Grafting proceeds on all types of AlOH groups without distinction. The presence of alkyl groups is confirmed by observation of C–H-related bands at 3000–2800 and 1460–1320 cm^{-1}. The solid-state ^{1}H NMR spectrum of **1** comprises a peak at $\delta = 0.8$ ppm, with a shoulder at $\delta = 1.8$ ppm, and the ^{13}C cross-polarization magic-angle spinning (CP MAS) NMR spectrum features a broad signal at $\delta = 28$ ppm.[6] The ^{27}Al MAS NMR spectrum is uninformative, as the signal of the bulk atoms masks the resonances from the grafted aluminum nuclei (see Figure S4a in the Supporting Information). Taking advantage of the presence of alkyl protons, one can make use of the HMQC correlation pulse sequence to gather information on their neighboring aluminum atoms. The dipolar-filtered ^{27}Al MAS NMR spectrum of **1** reveals only those aluminum centers spatially close to protons (see Figure S4b in the Supporting Information).[6] Setting the recoupling period at a small value

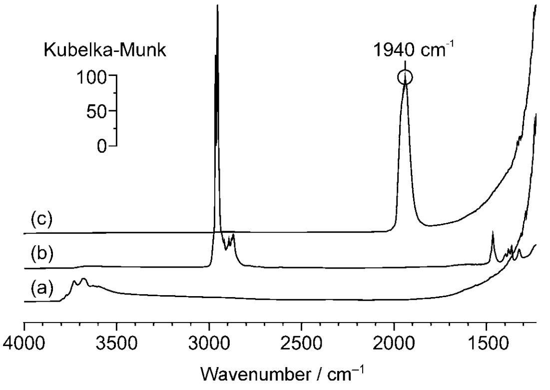


Figure 1. Infrared spectra of a) Al_2O_{3-500}, b) **1**, and c) **2**. The Kubelka-Munk model is used to describe diffuse reflectance.

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(500 μs) reduces the signal of the bulk alumina. The spectrum features a broad signal spreading from 100 to 0 ppm, resulting from four-, five-, and six-coordinated aluminum sites (Al_{IV}, Al_{V}, Al_{VI}) that are generally found at chemical-shift ranges of (100–40), (40–25), and (20–0) ppm, respectively.[8] Thus all three coordination types are presumably present within close vicinity to the alkyl fragments, mostly as Al*i*Bu groups but also as surface Al_2O_3 aluminum centers. The HMQC-filtered spectrum features an enhanced contribution in the Al_V region along with significant broadening of the Al_{IV} signal (see Figure S4b in the Supporting Information).[6] Despite poor resolution, it is likely that the Al_V electric field gradient, i.e. the C_Q value (quadrupole coupling constant), is in the upper range of the reported data. Similarly, the Al_{IV} resonance's broadening accounts for higher C_Q values than that encountered in the pristine material.[8] As high C_Q values are diagnostic of high dissymmetry, this indicates severe anisotropy of the Al coordination sphere.

Quantification of the isobutane released during the grafting step and a subsequent hydrolysis (550 and 1200 $\mu mol\,g^{-1}$, respectively) is consistent with the grafting of roughly 600 μmol of Al centers per gram. This is consistent with quasi-quantitative consumption of surface hydroxyls and with the above-postulated reaction pattern as the major grafting reaction scheme. If one considers the information extracted from the ^{27}Al HMQC NMR spectrum, several types of alkyl–aluminum coordination can originate either from protonolytic grafting, or from the transfer of alkyl groups onto acidic Al centers, accompanied with coordination by the oxygen atoms of the support, as observed in the well-documented reactivity of aluminum alkyls with silica surfaces.[9] At this stage, both the complexity of the proposed grafting chemistry and the insufficient selectivity of the dipolar HMQC sequence prevent clearer localization of alkyl groups.

Having introduced alkyl groups onto the surface, we set out to generate hydride groups by hydrogenolysis of the metal-carbon bond. We have extensively reported on surface transition-metal hydrides generated by this methodology.[2] However, main-group-metal alkyls display lower reactivity toward hydrogen: Examples of such reactions usually imply forcing conditions.[10] We reasoned that the strong polarization of the Al−C bond by the electron-deficient support would ease the heterolytic splitting of H_2. Prolonged heating of **1** at 400 °C under low H_2 pressure (0.733 bar) afforded material **2**. Formation of 4800 μmol of C in the gas phase per gram of **1** corresponds to 2.0 equivalents of isobutane per initially grafted Al center. In the absence of H_2, no reaction took place, which rules out the occurrence of β-H transfer and concomitant generation of isobutene and AlH. Hydrogenolysis starts at lower temperatures (250 °C) and is complete at 400 °C. The formation of the corresponding amount of hydride is indicated by the stoichiometry of the hydrolysis, as 1200 μmol of H_2 are released upon exposure of **2** to excess water. In the infrared spectrum of **2**, the characteristic $\nu_{(AlH)}$ signals appear at 1940 cm^{-1},[4] while those of the *i*Bu groups almost completely vanish (Figure 1 c). Performing the reaction under D_2 led to the formation of a $\nu_{(AlD)}$ band with the expected isotopic shift (1400 cm^{-1}).

Figure 2 a,b shows the ^{1}H MAS NMR spectrum of **2** at two static magnetic fields (9.4 and 18.8 T). The main spectral feature is a multiplet centered at about 3.5 ppm, arising from the indirect spin–spin coupling with a spin 5/2 nucleus like ^{27}Al. Figure 2 c is a *J*-HMQC-filtered ^{1}H MAS spectrum obtained with an ^{27}Al rotor-asynchronized multiple-pulse (RA-MP) decoupling,[11] revealing the ^{1}H chemical-shift region of the hydride species. The spectrum reveals the presence of a ^{1}H site at a chemical shift of $\delta = 3.3$ ppm, in a major proportion. This chemical shift lies below the expected range for molecular aluminum hydrides,[12] but is similar to what was observed in related materials.[13] The unusual asymmetric pattern observed in the non-decoupled ^{1}H MAS spectra at two magnetic fields results from contributions of 1) the scalar coupling J_{iso} and 2) a second-order coupling arising from the strong dipolar/quadrupolar cross term between ^{1}H and ^{27}Al.[14] The spacing of 376 Hz between the innermost lines in Figure 2 a is a direct measure of the ^{1}H–^{27}Al scalar coupling. This J_{iso} value, higher than those reported so far,[15] denotes the specificity of the present hydride species. The interval between the outer lines of the multiplet is inversely proportional to the aluminum Larmor frequency ν_{Al}, which explains the larger spreading of the multiplet observed at 9.4 T with respect to that observed at 18.8 T. It is also directly proportional to the quadrupolar coupling constant C_Q and the dipolar constant D_{IS}. From crystallographic data, it is reasonable to consider the Al–H distance to be greater than 1.50 Å,[12] which leads to a dipolar coupling constant of about 9 kHz. A fair simulation of the spectrum points to high values of C_Q of about 15 MHz (see Figure S5 in the Supporting Information), much larger than values commonly reported,[8] but in line with those encountered for silica-supported aluminum alkyls.[9] This large C_Q value directly reflects the large electric field gradient that is present around the considered Al–H unit. Therefore, the unprecedented large splitting observed in Figure 2 corresponds to a high local dissymmetry around the aluminum: Surface heterogeneity enforces a highly distorted first coordination sphere. This is not surprising as hydride species derive from

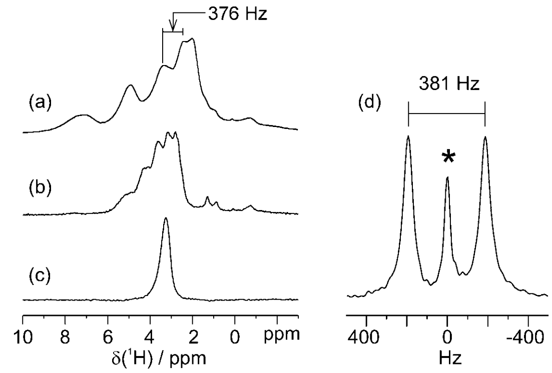

Figure 2. ^{1}H MAS NMR spectra of **2** recorded at a) $B_0 = 9.4$ T and b) $B_0 = 18.8$ T. c) *J*-HMQC-filtered ^{1}H MAS spectrum with ^{27}Al RA-MP decoupling ($B_0 = 18.8$ T). d) *J*-resolved slice[6] ($B_0 = 18.8$ T). For comments on the central peak (*), see the Supporting Information.

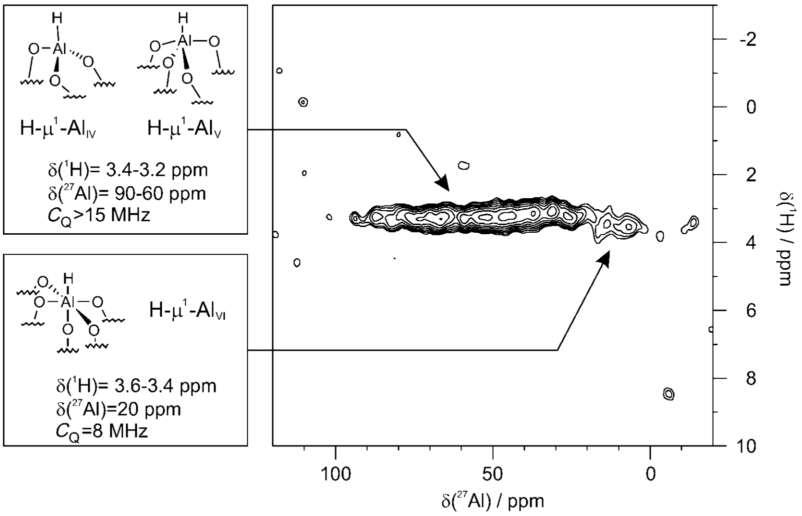

Figure 3. ^{27}Al–^{1}H *J*-HMQC MAS NMR spectrum of **2**.[6]

hydrogenolysis of the alkyl-substituted Al$_{IV/V}$ centers in **1**, which themselves feature large C_Q values.

A *J*-resolved NMR experiment[16] in which an ^{27}Al π pulse is used to express the heteronuclear *J* coupling during a ^{1}H spin-echo, was performed with material **2**. The signal presented in the frequency domain in Figure 2d clearly corresponds to a doublet characteristic of a terminal aluminum hydride with a separation of 381 Hz, in line with the scalar coupling J_{iso} measured in the ^{1}H MAS spectrum.

The ^{27}Al–^{1}H correlation spectrum in Figure 3 was acquired using the *J*-HMQC pulse sequence, which correlates nuclei through their scalar coupling, a method well suited for hydride species presenting large $^{1}J_{Al\text{-}H}$ couplings.[15] The broad signal along the ^{27}Al dimension correspond to only those aluminum centers bearing hydride ligands. This spectrum confirms the predominance of highly distorted (i.e. with large C_Q values) Al$_{IV/V}$–H units in **2**, although no conclusion can be drawn regarding the absolute proportion of Al$_{V}$ in **2**. The proportion of Al$_{VI}$–H is small in **2** (estimated to be less than 10%), as in **1**, where Al$_{VI}$–*i*Bu species were assumed to be present in much weaker proportion than the tetra- and pentacoordinated aluminum alkyl centers. In the Al$_{VI}$ case, the quadrupolar broadening is clearly reduced, indicating a comparatively more symmetrical environment. Interestingly, as the Al$_{IV/V}$–H species gives ^{1}H NMR signals in the (3.4–3.2) ppm range, the Al$_{VI}$–H hydrides resonate at lower fields ((3.6–3.4) ppm). The NMR characteristics for the identified types of hydrides are summarized in Figure 3.

Finally, exposure of material **2** to ethylene leads to the formation of polyethylenic fragments and the disappearance of of Al–H bands in the in situ IR spectrum recorded immediately after the reaction (100 °C, 0.733 bar).[6] Performing the reaction under forcing conditions (30 bar C_2H_4, 100 °C) afforded polyethylene with an activity of 550 $g_{PE}\,mol_{AlH}^{-1}\,h^{-1}\,bar^{-1}$. The resulting polymer is a ultra-high-molecular-weight linear polyethylene with a mass distribution characteristic of single-site polymerization ($M_n = 8.7 \times 10^5\,g\,mol^{-1}$, $M_w/M_n = 2.7$). As this demonstrates that these surface aluminum hydrides are reactive toward double-bond insertion, and as we have shown that Al–C bonds can be cleaved through H_2 heterolytic cleavage, we reasoned that these two elementary steps (olefin insertion followed by Al–C hydrogenolysis) may be combined into overall olefin hydrogenation. Indeed, exposure of ethylene and H_2 to **2** in a continuous-flow reactor (H_2 and C_2H_4: 4 mL min^{-1}, 400 °C) resulted in sustained conversion into ethane, while Al_2O_{3-500} proved inactive under identical conditions. This represents the first example of the hydrogenation of inactivated olefins by aluminum, which parallels recent findings in alkaline-earth-metal catalysis[17] and catalysts based on main-group-metal frustrated Lewis pairs.[18] The reactivity of material **2** most likely owes a lot to the peculiar structure of the supported hydrides, as is evident from their NMR features. Indeed, the uncommon highly strained molecular structure may well be the source of this unprecedented reactivity; we are currently exploring the potential of this cheap and easily accessible catalytic material in strategic alkene transformations.

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