

Electronic Supporting Information

Titanium Methyl Tamed on Silica: Synthesis of a Well-defined Pre-catalyst for Hydrogenolysis of n-alkane

Aya Saidi, ^a Walid Al Maksoud, ^a Manoja K. Samantaray, ^{*a} Edy Abou-Hamad, ^b and Jean-Marie Basset ^{*a}

[a] King Abdullah University of Science & Technology, Physical Science and Engineering, KAUST, Thuwal, 23955-6900, Saudi Arabia. E-Mail: jeanmarie.basset@kaust.edu.sa, manoja.samantaray@kaust.edu.sa

[b] Imaging and Characterization Core lab, King Abdullah University of Science and Technology, KAUST, Thuwal, 23955-6900, Saudi Arabia

Table of Contents

1. Experimental Section	3
1.1. General Procedures	3
1.2. Preparation of $\text{Ti}(\text{CH}_3)_4$ (Complex 2)	3
1.3. Preparation of ^{13}C -enriched MeLi	4
1.4. Preparation of Silica Partially Dehydroxylated at 700 °C (SiO_{2-700})	4
1.5. Grafting of $\text{Ti}(\text{CH}_3)_4$ onto SiO_{2-700} (Complex 3).....	4
1.6. Hydrolysis of Complex 3.....	4
1.7. IR Spectroscopy.....	5
1.8. Elemental analyses.....	5
1.9. Liquid-State Nuclear Magnetic Resonance Spectroscopy.....	5
1.10. Solid-State Nuclear Magnetic Resonance Spectroscopy	5
1.11. GC Analysis	7
1.12. Hydrogenolysis Reaction	7
2. Supporting Figures	8

1. Experimental Section

1.1. General Procedures

All experiments were carried out by using standard Schlenk and glovebox techniques under an inert argon atmosphere. The syntheses and the treatments of the surface species were carried out using high vacuum lines ($< 10^{-5}$ mbar). Pentane was distilled from a Na/K alloy under Ar and dichloromethane from CaH_2 . Both solvents were degassed through freeze-pump-thaw cycles. TiCl_4 , $\text{Zn}(\text{CH}_3)_2$ (1.0 M in heptane), $\text{CH}_3(\text{CH}_2)_3\text{Li}$ (2.5 M in hexanes), and ^{13}C -enriched CH_3I were purchased from Sigma Aldrich. Hydrogen (99.9999%), argon (99.999%), propane (99.999%), *n*-butane (99.95%) and calibration mixture (Helium 8%, methane 6%, ethane 5%, propane 3%, *n*-butane 100 ppm, *n*-pentane 100 ppm, hexane 100 ppm, heptane 100 ppm, octane 100 ppm, and decane 100 ppm) gases were purchased from Specialty Gases Center of Abdullah Hashim Industrial Gases & Equipment Co. Ltd. (Saudi Arabia). Propane and *n*-butane cylinders were connected successively to Agilent Gas Clean moisture, and Agilent Gas Clean oxygen filters before the mass flow controllers of the reactor. Argon and Hydrogen cylinders were connected to Thermo Scientific Triple filters (Oxygen, Moisture, Hydrocarbons) before the mass flow controllers of the reactor.

1.2. Preparation of $\text{Ti}(\text{CH}_3)_4$ (Complex 2)

The molecular precursor TiCl_4 (0.25 mL, 2.28 mmol) is mixed with one equivalent of $\text{Zn}(\text{CH}_3)_2$ (1.0 M in heptane) in a mixture of pentane (5 mL) and dichloromethane (5 mL) under stirring at -80 °C for one hour. Then the reaction mixture was warmed up to -40 °C for 3 hours, forming an orange color of $\text{TiCl}_2(\text{CH}_3)_2$ (Complex 1). The mixture was kept in the freezer at -40 °C for two days to settle down all the dissolved salt. Later, the mixture was filtered and reacted with an excess of MeLi (50 % enriched) at -80 °C and let the reaction continues for one hour at that temperature. Slowly, the temperature increases to -60 °C and continue the reaction for another 3 hours at that temperature. At the end of the reaction, the mixture was filtered and characterized as a red color viscous substance of $\text{Ti}(\text{CH}_3)_4$ (Complex 2) with a yield $\approx 55\%$.

1.3. Preparation of ^{13}C -enriched MeLi

In a 200 mL Schlenk under argon, 2 mL of ^{13}MeI diluted in 30 mL of pentane were introduced, then 13 mL of n-butyllithium solution (2.5 M in hexanes) were added dropwise at $-20\text{ }^\circ\text{C}$ with stirring for 1 hour, a white precipitate started to form immediately. Then, the solution was warmed up to room temperature and stirred for another two days. The precipitate was then filtered and dried under vacuum to produce a white solid ($^{13}\text{MeLi}$).

1.4. Preparation of Silica Partially Dehydroxylated at $700\text{ }^\circ\text{C}$ (SiO_{2-700})

SiO_{2-700} is prepared from Aerosil silica from Degussa (specific area of $200\text{ m}^2/\text{g}$), it was partially dehydroxylated at $700\text{ }^\circ\text{C}$ under high vacuum ($< 10^{-5}\text{ mbar}$) for 24 h to give a white solid having a specific surface area of $190\text{ m}^2/\text{g}$ and containing around 0.3 mmol OH/g .

1.5. Grafting of $\text{Ti}(\text{CH}_3)_4$ onto SiO_{2-700} (Complex 3)

Complex **3** is formed following the SOMC strategy; an excess of **2** in pentane (1.2 equivalent with respect to the amount of surface accessible silanols; $\approx 0.3\text{ mmol of OH groups per gram}$) was reacted with 1 g of SiO_{2-700} under stirring at $-60\text{ }^\circ\text{C}$ for 4 h. At the end of the reaction, the resulting dark brown solid was filtered, washed with pentane ($3 \times 20\text{ mL}$), and dried under a dynamic high vacuum ($<10^{-5}\text{ mbar}$) for 1 h then stored in the freezer ($-40\text{ }^\circ\text{C}$).

1.6. Hydrolysis of Complex 3

A sample of **3** (50 mg, 1.8% of Ti) was transferred in a Schlenk tube (180 mL), to this degassed water vapor (0.5 mL) was added and allowed to react with **3** at room temperature for 2 h. An aliquot of the gas mixture was released and analyzed by gas chromatography, only methane was detected, 0.937 mmol/g of methane were quantified by GC (theoretically, we should get 1.065 mmol/g for monopodal species) which is consistent with the formation of $[(\equiv\text{SiO-})\text{TiMe}_3]$ surface species.

1.7. IR Spectroscopy

IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer by using a DRIFT cell equipped with CaF₂ windows. The IR samples were prepared under argon within a glovebox. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm⁻¹).

1.8. Elemental analyses

Elemental analyses were performed at Core Lab ACL KAUST.

1.9. Liquid-State Nuclear Magnetic Resonance Spectroscopy

All liquid-state NMR spectra were recorded on Bruker Avance 600 MHz spectrometers. All chemical shifts were measured relative to the residual ¹H or ¹³C resonance in the deuterated solvent CD₂Cl₂; 5.32 ppm for ¹H and 53.5 ppm for ¹³C.

1.10. Solid-State Nuclear Magnetic Resonance Spectroscopy

- **One-dimensional ¹H MAS and ¹³C CP-MAS solid-state NMR:** The spectra were recorded on a Bruker AVANCE III spectrometer operating at 600 or 400 MHz ¹H resonance frequencies, with a conventional double resonance 3.2 or 4mm CPMAS probe. The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 22 and 10 kHz for ¹H, ¹³C spectra, respectively. NMR chemical shifts are reported with respect to TMS as an external reference. For CP/MAS ¹³C NMR, the following sequence was used: 90° pulses on the proton (pulse length 2.4 s), then a cross-polarization step with a contact time typically 2 ms, and finally the acquisition of the ¹³C signal under high-power proton decoupling. The delay between the scan was set to 5 s, to allow the complete relaxation of the ¹H nuclei and the number of scans was between 10,000-20,000 for carbon, and 32 for proton. An apodization function (exponential) corresponding to a line broadening of 80 Hz was applied before Fourier transformation.
- **Two-dimensional ¹H-¹³C heteronuclear correlation (HETCOR):** Solid-state NMR spectroscopy experiments were conducted on a Bruker AVANCE III spectrometer using a

4 mm MAS probe. The experiments were performed according to the following scheme: 90° proton pulse, t_1 evolution period, cross-polarization (CP) to carbon spins, and detection of carbon magnetization under TPPM decoupling. For the cross-polarization step, a ramped radio frequency (RF) field centered at 75 kHz was applied to protons, while the carbon RF field was matched to obtain an optimal signal. A total of 64 t_1 increments with 2048 scans were collected. The sample spinning frequency was 10 kHz. A 2D Fourier transformation gives through space between pairs of neighboring carbon (in F2) and proton (in F1) nuclei. Using a short contact time (0.2 ms) for the CP step, the polarization transfer in the dipolar correlation experiment is expected to be quite selective, that is to lead to correlation only between pairs of attached ^1H - ^{13}C spins (C-H directly bonded).

- **^1H - ^1H multiple-Quantum Spectroscopy:** Two-dimensional double-quantum (DQ) and triple-quantum (TQ) experiments were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz with a conventional double resonance 3.2 mm CPMAS probe, according to the following general scheme: excitation of DQ coherences, t_1 evolution, Z-filter, and detection. The spectra were recorded in a rotor synchronized fashion in t_1 ; that is the t_1 increment was set equal to one rotor period (4.545 μs). One cycle of the standard back-to-back (BABA) recoupling sequence was used for the excitation and reconversion period. Quadrature detection in w_1 was achieved using the States-TPPI method. A spinning frequency of 22 kHz was used. The 90° proton pulse length was 2.5 μs , while a recycle delay of 5 s was used. A total of 128 t_1 increments with 128 scans each were recorded. Double (DQ)- and Triple (TQ)-quantum proton spectroscopies under fast MAS have recently shown to be powerful techniques to probe the structural information and dynamics inherent proton-proton dipolar couplings. The DQ frequency in the w_1 dimension corresponds to the sum of two single quantum (SQ) frequencies of the two coupled protons and correlates in the w_2 dimension with the two corresponding proton resonances. The TQ frequency in the w_1 dimension corresponds to the sum of the three SQ frequencies of the three coupled protons and correlates in the w_2 dimension with the three individual proton resonances. Conversely, groups of less than three equivalent spins

will not give rise to diagonal signals in the spectrum. Two-dimensional DQ and TQ correlations experiments can thus apply to determine in a reliable way the number of the attached equivalent proton.

1.11. GC Analysis

The gas products were analyzed every 20 min by online gas chromatography using a Varian 450-GC system with a flame ionization detector (FID) for the analysis of hydrocarbons.

Column: GS-GASPRO, 30 m length, 0.32 mm diameter (Agilent J&W GC Columns).

Method: Front injector setpoint 150 °C, oven 40 °C hold for 2 min followed by 10 °C/min rate up to 180 °C hold for 1 min. TCD heater setpoint 180 °C, filament temperature 225 °C. FID setpoint 250 °C. The Split ratio is 20 initially, then increased to 100 from 0.5 to 5 min, then decreased to 20 after 5 min.

The GC was calibrated using a calibration mixture of mixed hydrocarbons to qualify and quantify the reactants and the formed products. The response and retention time for each component of the calibration mixture was established based on three independent runs.

1.12. Hydrogenolysis Reaction

The catalytic hydrogenolysis of propane and n-butane was performed on a micro-pilot (PID Eng&Tech) equipped with a stainless steel reactor operating at atmospheric pressure. The catalyst powder was placed in the reactor supported by dried quartz wool. Conversions were calculated based on carbon mass balance.

Complex **3** (0.088 mmol) was loaded in a glovebox into a 0.5 inch diameter stainless steel reactor fitted with a four-channel isolating valve. After connection to the rack, all the tubing were purged bypassing the reactor with argon flow (20 mL/min) for 30 min, then with the reaction mixture (3.6 mL/min of propane or n-butane and 9 mL/min of hydrogen) for additional 10 min. Then the four-channel valve was switched on, and the reactor was heated to 180 °C (4°C /min) at 1 atm. The gaseous products were analyzed online with the connected GC.

2. Supporting Figures

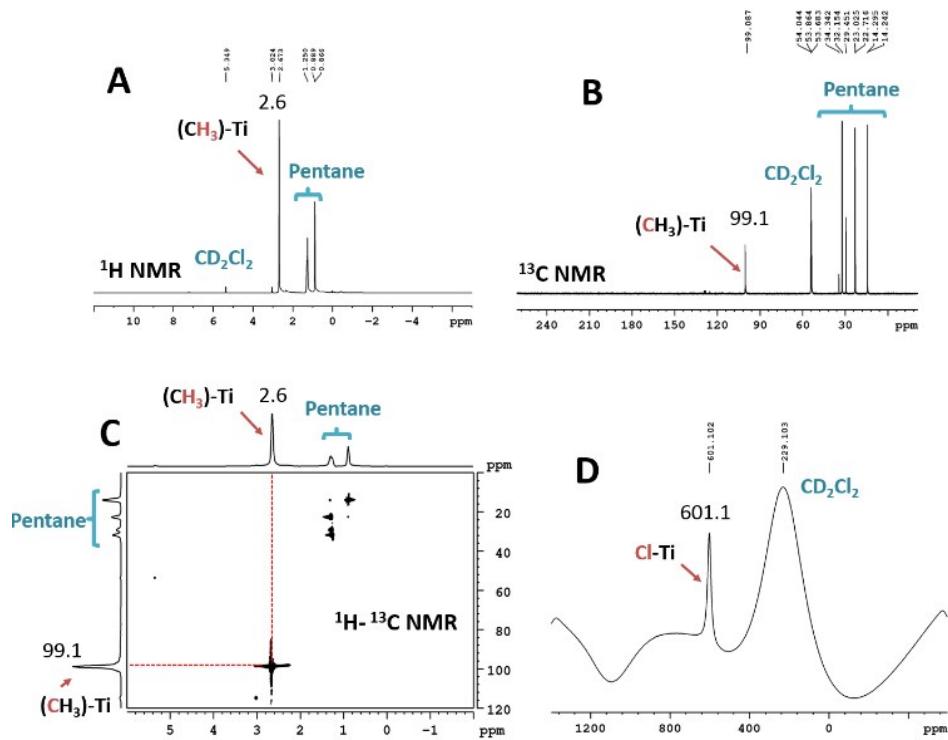


Figure S1. (A) ^1H , (B) ^{13}C , (C) HSQC, and (D) ^{35}Cl NMR spectra of $\text{Ti}(\text{CH}_3)_2\text{Cl}_2$ in CD_2Cl_2 at 233 K

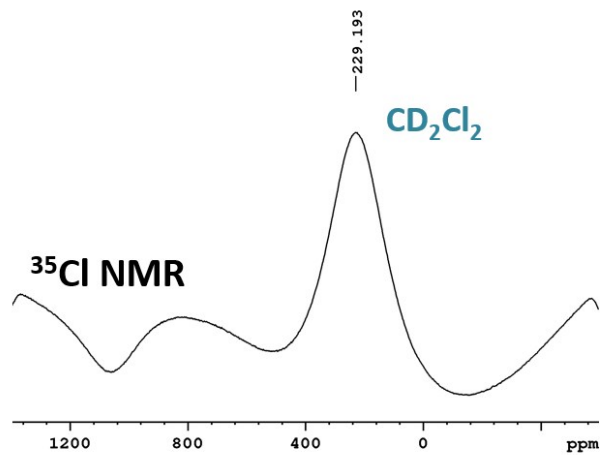


Figure S2. ^{35}Cl NMR spectra of $\text{Ti}(\text{CH}_3)_4$ in CD_2Cl_2 at 213 K

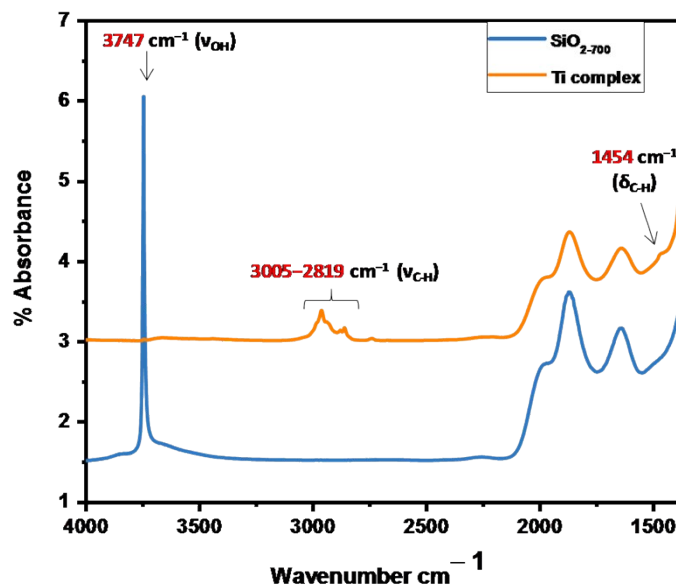
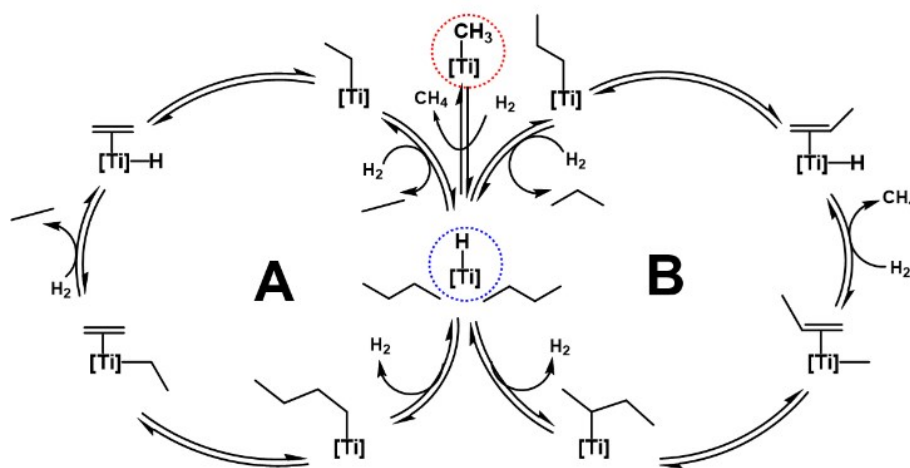


Figure S3. FT-IR spectra of silica partially dehydroxylated at 700 °C (Blue curve) and grafted $\text{Ti}(\text{CH}_3)_4$ complex on silica **3** (Orange curve).



Scheme S1. A proposed mechanism of hydrogenolysis with pre-catalysts **3** either by activating the C-H bond of the terminal (**A**) or secondary (**B**) carbon of the alkane