Supporting Information

Non Oxidative Coupling Reaction of Methane to Ethane and Hydrogen Catalysed by the Silica-Supported Tantalum Hydride: $(\equiv SiO)_2Ta\text{-}H$.

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Experimental Section.

General procedure. All experiments were carried out under controlled atmosphere, using Schlenk and glove box techniques for preparation or handling of organometallic compounds. The silica supported tantalum hydride was prepared as already reported. [10]

Conversion of methane into ethane in a continuous flow reactor. The tantalum hydride $(\equiv SiO)_2Ta\text{-}H$, **1** (300 mg; 5,35 wt% Ta) was charged using a glove box, into a stainless steel ½" cylinder reactor which can be isolated from atmosphere. After connection to the gas lines and purge of tubes, a flow of methane controlled by a "Brooks" mass flow-meter was sent under 50 bars, with a flow rate of 3 ml/min (or WHSV = 0.44 h^{-1}), onto the catalyst bed heated at a constant temperature between 250°C and 475°C. Hydrocarbon products and hydrogen were analyzed on line by GC (Varian CP 4900 micro-GC fitted with10 m x 0.32 mm capillary columns: an Al_2O_3/KCl, for hydrocarbons and a molecular sieve 5A, for hydrogen, both with a catharometer detector).

Temperature programmed reaction (TPRn) of methane on tantalum hydride $(\equiv SiO)_2Ta\text{-}H$, 1. A procedure quite similar to that described above for the catalytic reaction was used, but with a temperature ramp of 10°C/h between 25 and 375°C for the experiment under 1 bar and a temperature ramp of 50°C/h between 25 and 475°C for the experiment under 50 bars.

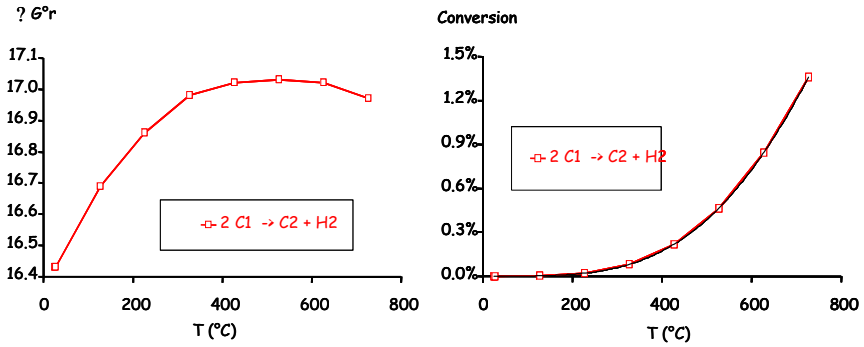

Figure S1: Thermodynamic data (Gibbs energy and corresponding equilibrium conversion vs temperature) of the non oxidative coupling reaction of methane.

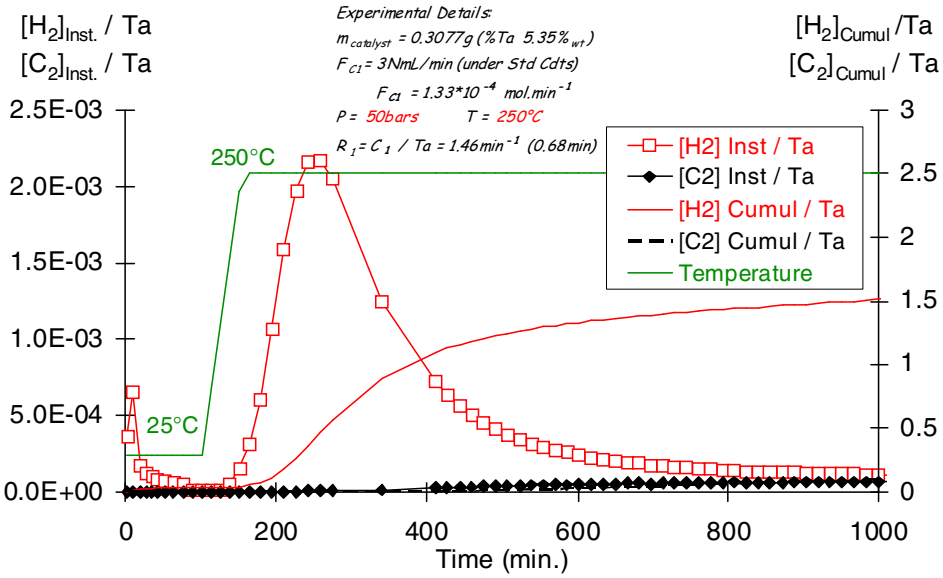

Figure S2: Evolution of products during the initiation period of the non oxidative coupling reaction of methane catalysed by $(\equiv SiO)_2Ta\text{-}H$, **1**.

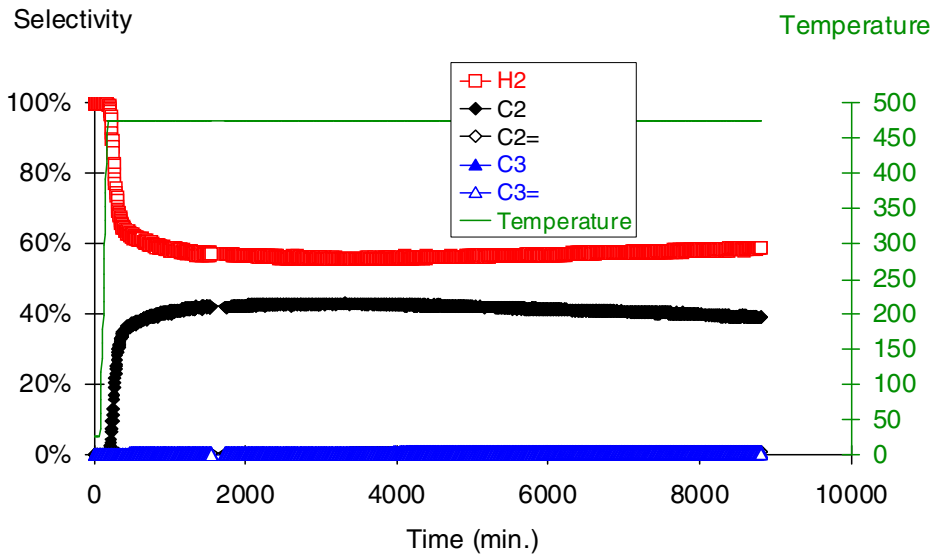

Figure S3: Selectivity obtained at 475°C in the non oxidative coupling reaction of methane catalysed by the silica supported tantalum hydride $(\equiv SiO)_2Ta\text{-}H$, **1**.

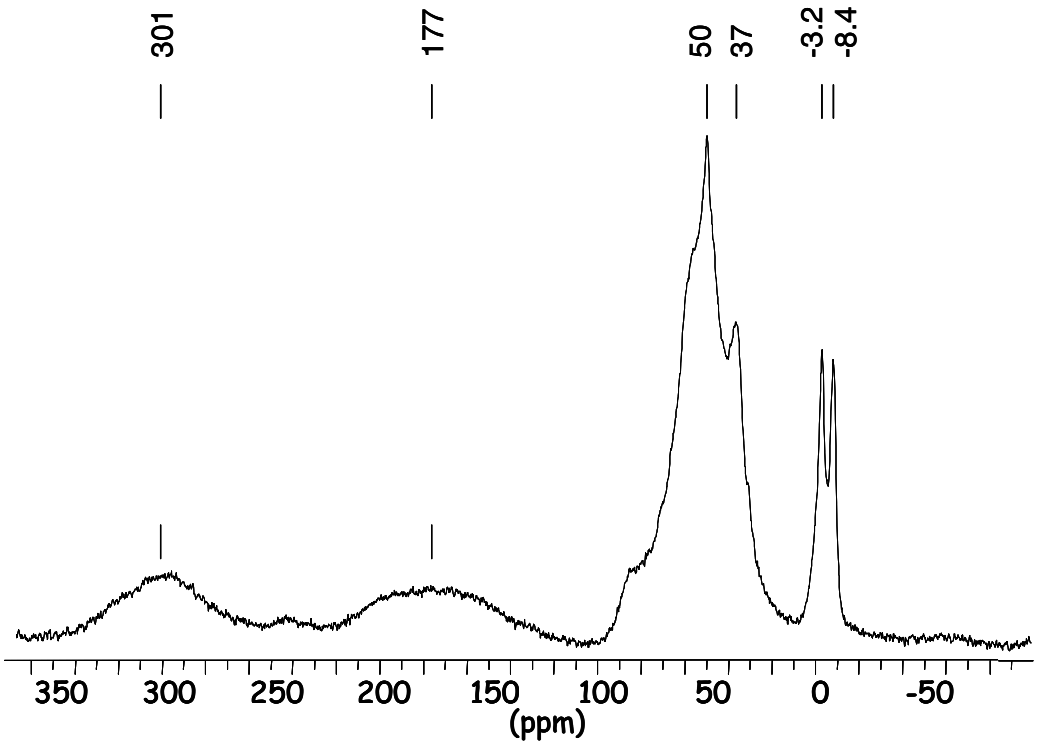

Figure S4: ^{13}C solid state NMR of $^{13}CH_4$ activated at 250°C for 22h, on the tantalum hydride $(\equiv SiO)_2Ta\text{-}H$, **1** supported on MCM-41 ($^{13}CH_4/Ta = 90$).

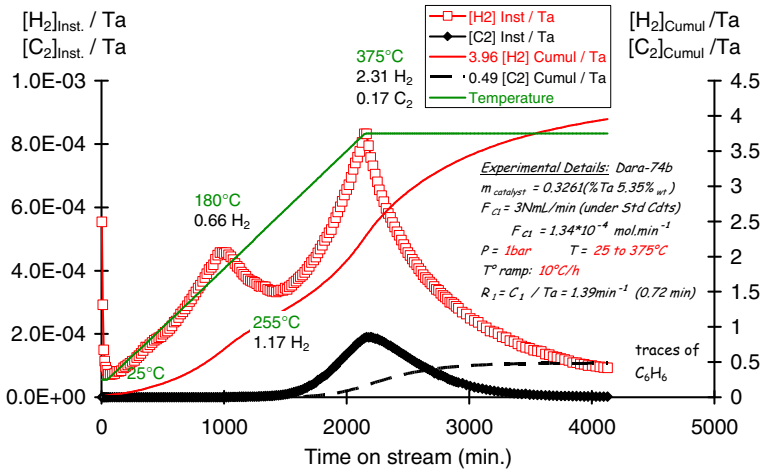

Figure S5: Temperature programmed reaction (TPRn) of methane (3ml/min, 1bar, 25-375°C, 10°C/h) on the tantalum hydride (≡SiO)$_2$Ta-H, **1** (0.32g; 5.35 wt% Ta).

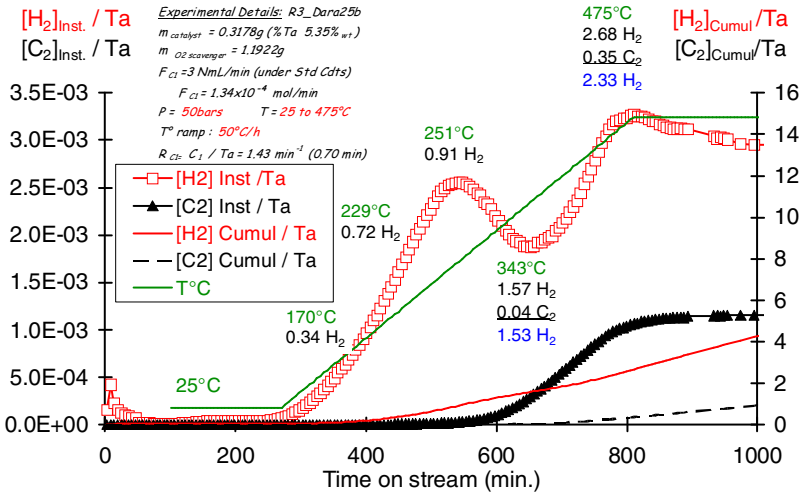

Figure S6: TPRn of methane (3ml/min, 50bars, 25-475°C, 50°C/h) on the tantalum hydride (≡SiO)$_2$Ta-H, **1** (0.32g; 5.35 wt% Ta).