

Supplementary Material

Non-Oxidative Coupling of Methane Catalysed by Supported Tungsten Hydride onto Alumina and Silica-Alumina in a Classical and H₂ Permeable Membrane Fixed-Bed Reactors

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Experimental Details

General procedures. All experiments were carried out under controlled atmosphere, using Schlenk techniques and glove box for preparation or handling of organometallic compounds. γ -Alumina and silica-alumina were purchased from Degussa and Akzo-Nobel, respectively. γ -Alumina and silica-alumina supported tungsten hydride were prepared as already reported.^{1,2}

IR spectra were recorded on a Nicolet 550-FT spectrophotometer in transmission mode by using an infrared cell equipped with CaF₂ windows, allowing *in situ* studies. Solid-state NMR spectra were recorded on a Bruker DSX-300 spectrometer equipped with a standard 4-mm double-bearing probe head and operating at 75.47, 300.18 MHz for ¹³C and ¹H respectively.

Representative catalytic conversion of methane procedure. In a glove box, the tungsten hydride supported on γ -alumina (500 mg; 4 wt% W) or silica-alumina (300 mg; 7 wt% W) were loaded into a stainless steel 1/2" cylinder reactor and the amount of catalyst was adjusted to be 1.2 mol_{CH₄} mol_W⁻¹ min⁻¹. Catalytic conversion of methane was carried out in fixed-bed type stainless steel reactors at 350°C and 50 bar which was connected to a Varian CP-4900 μ -GC for product determination (fitted with 10 m x 0.32 mm capillary columns: an Al₂O₃/KCl, for hydrocarbons and a molecular sieve 5 Å, for hydrogen, both with a catharometer detector). Only pure methane (purity 99.999%, from air liquid) was fed through the reactor at 3 mL min⁻¹. For the fixed-bed reactor equipped with the H₂ selective membrane based on Pd-Ag, the membrane was purchased from *REB Research & Consulting*. The membrane was installed as high pressure cylindrical tubes in the metallic reactor. Hence, the catalyst surrounded the membrane tubes. Catalytic conversion occurred when methane was flowed through the reactor. Hydrogen produced from the reaction diffused selectively through the membrane tubes and then removed by a sweep gas (argon was used). Additional experiments suggested that the optimal permeability was to apply a self supported pressure of the sweep gas at 30 bars and a flow rate at 30 ml min⁻¹.

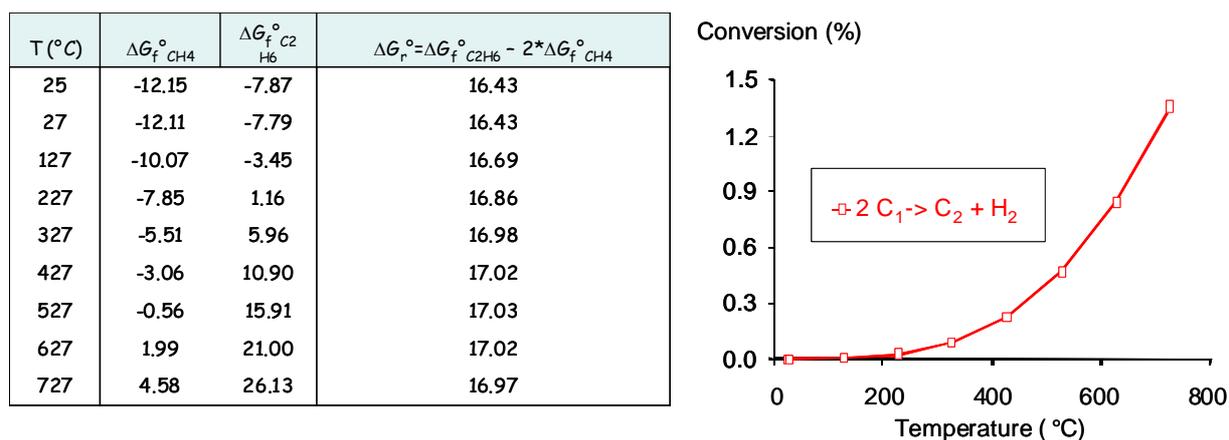


Fig. S1 Thermodynamic data (Gibbs energy and corresponding equilibrium conversion *versus* temperature) of the NOCM reaction.

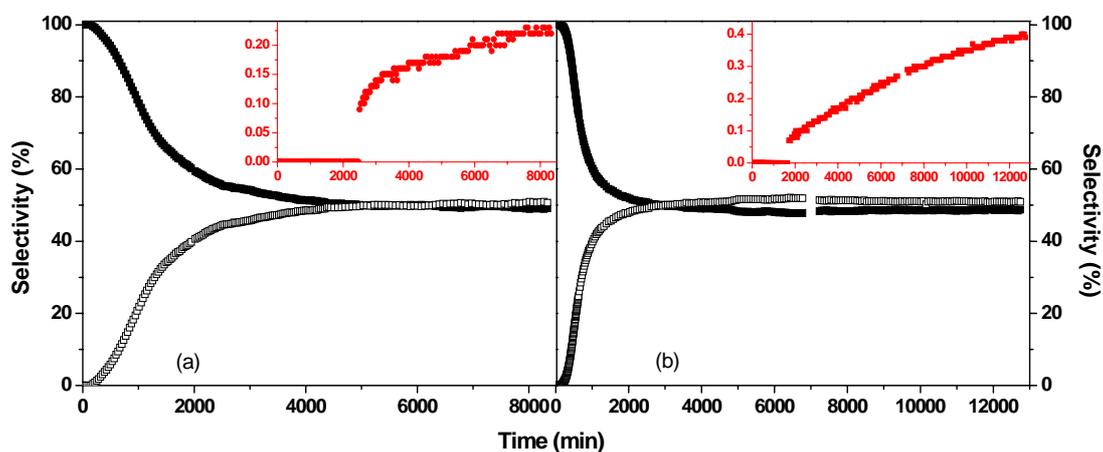


Fig. S2 Product distribution of NOCM catalysed by (a) W-H@SiO₂-Al₂O₃ and (b) W-H@ γ -Al₂O₃ (top black curve: H₂; bottom black curve C₂; red curves: C₃ selectivity).

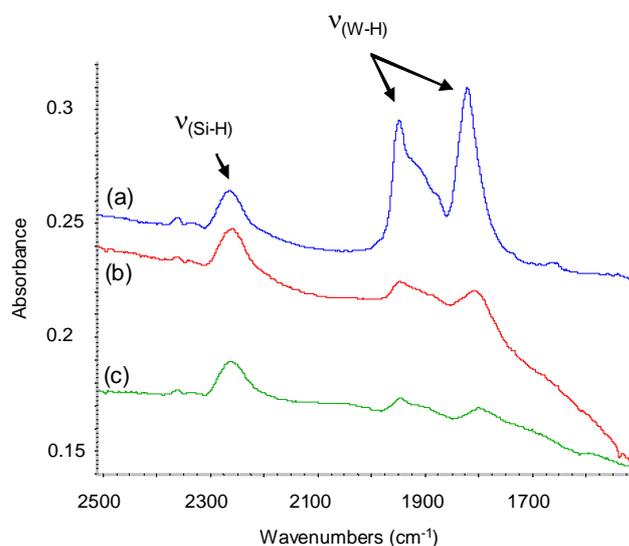


Fig. S3 Activation of CH_4 at 150°C on $\text{W-H@SiO}_2\text{-Al}_2\text{O}_3$ monitoring by *in situ* IR spectroscopy. (a) $\text{W-H@SiO}_2\text{-Al}_2\text{O}_3$. (b) After activation of CH_4 at 150°C on $\text{W-H@SiO}_2\text{-Al}_2\text{O}_3$ during 5 h. (c) (b) After activation of CH_4 at 150°C on $\text{W-H@SiO}_2\text{-Al}_2\text{O}_3$ during 24 h.

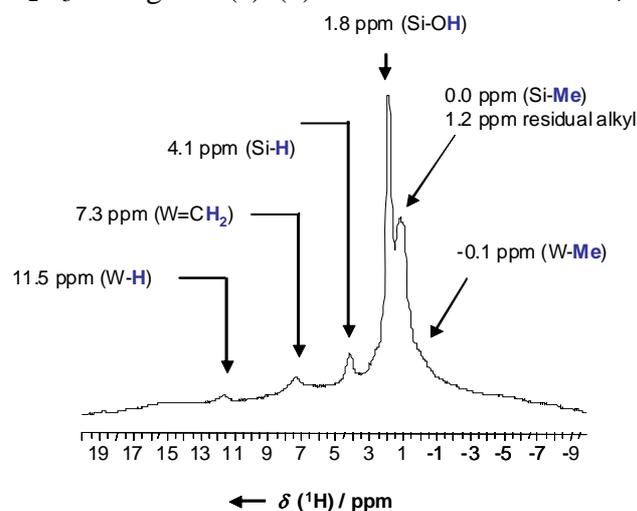


Fig. S4 Solid-state ^1H MAS NMR spectra of $\text{W-H@SiO}_2\text{-Al}_2\text{O}_3$ obtained after $^{13}\text{CH}_4$ activation at 150°C during 24 h (NS 8, D1 = 1 s, LB = 0 Hz).

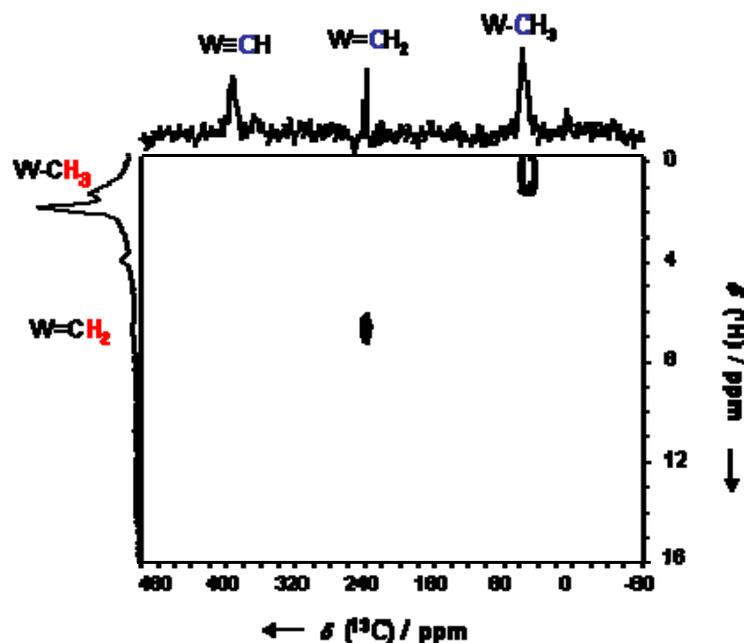


Fig. S5 ^1H - ^{13}C HETCOR solid-state NMR spectrum of $\text{W-H@SiO}_2\text{-Al}_2\text{O}_3$ obtained after $^{13}\text{CH}_4$ activation at 150°C during 24 h (NS 2048, D1 = 1 s, P15 = 5 ms, LB = 50 Hz).

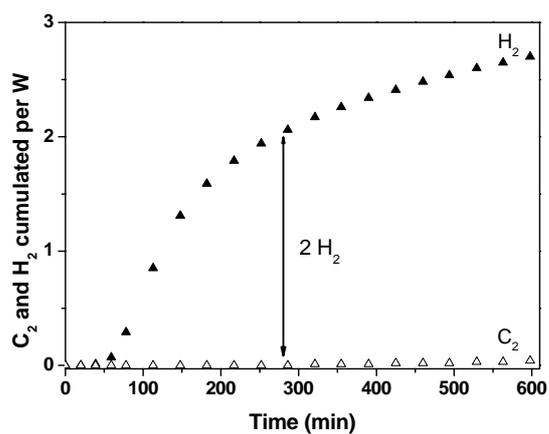


Fig. S6 Evolution of products during the initiation period of the NOCM catalysed by W-H@SiO₂-Al₂O₃.

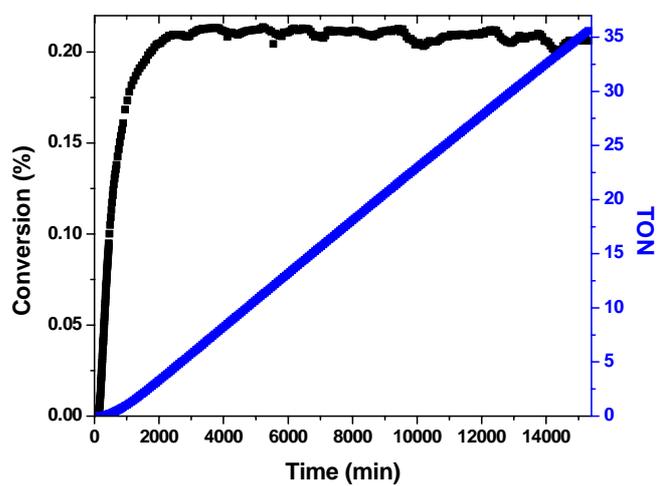


Fig. S7 Catalytic performance of W-H@Al₂O₃ in a fixed-bed reactor for long time.

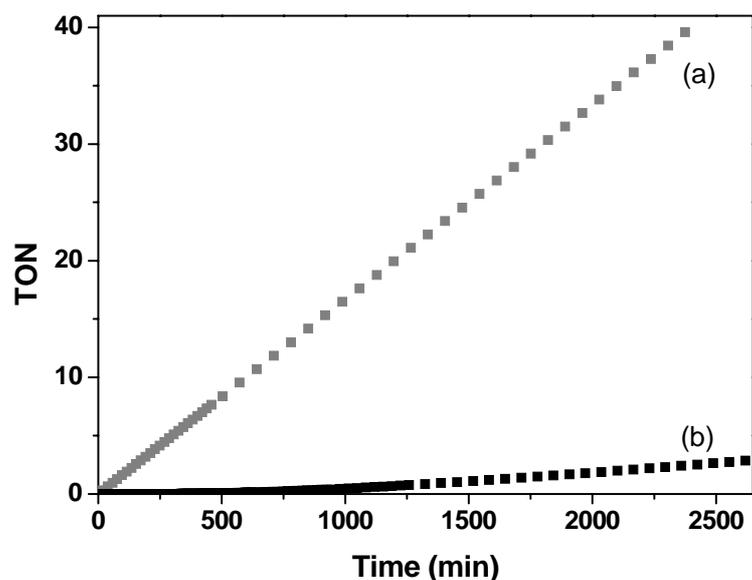
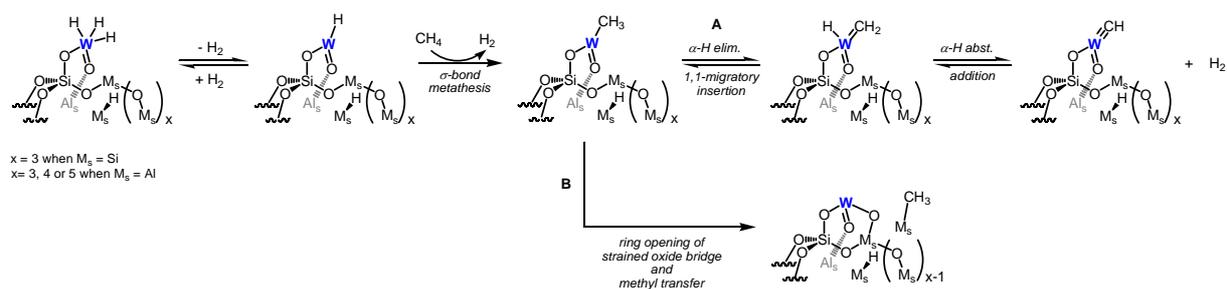


Fig. S8 Catalytic performances of W-H@ γ -Al₂O₃ (a) equipped with Pd-Ag membrane and (b) without Pd-Ag membrane in a fixed-bed reactor for the NOCM.



Scheme S1 A) Reaction pathway leading to [W(=O)(Me)], by activation of CH₄ onto W-H@SiO₂-Al₂O₃, and then to [W(=O)(=CH₂)(H)] and [W(=O)(≡CH)] by subsequent α -H elimination and α -H abstraction. B) Reaction pathway leading to the formation of [(≡SiO)(M_s)W(=O)] species along with (M_s-Me) fragment upon treatment of W-H@SiO₂-Al₂O₃ under CH₄ at 150°C.

¹ E. Le Roux, M. Taoufik, C. Copéret, A. de Mallmann, J. Thivolle-Cazat, J. M. Basset, B. M. Maunders and G. J. Sunley, *Angew. Chem. Int. Ed.*, 2005, **44**, 6755-6758.

² E. Le Roux, M. Taoufik, A. Baudouin, C. Copéret, J. Thivolle-Cazat, J. M. Basset, B. M. Maunders and G. J. Sunley, *Adv. Synth. Catal.*, 2007, **349**, 231-237.