

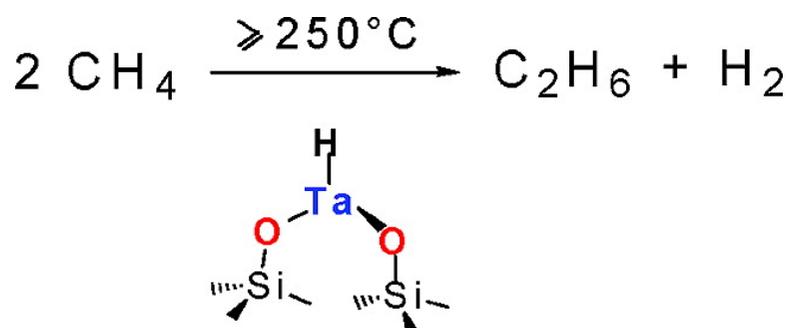
Communication

**Non-Oxidative Coupling Reaction of Methane to Ethane and Hydrogen
 Catalyzed by the Silica-Supported Tantalum Hydride: (#SiO)Ta#H**

Daravong Soulivong, Sebastien Norsic, Mostafa Taoufik, Christophe
 Cope#ret, Jean Thivolle-Cazat, Sudhakar Chakka, and Jean-Marie Basset

J. Am. Chem. Soc., **2008**, 130 (15), 5044-5045 • DOI: 10.1021/ja800863x • Publication Date (Web): 26 March 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Non-Oxidative Coupling Reaction of Methane to Ethane and Hydrogen Catalyzed by the Silica-Supported Tantalum Hydride: $(\equiv\text{SiO})_2\text{Ta}-\text{H}$

Daravong Soulivong,[†] Sébastien Norsic,[†] Mostafa Taoufik,[†] Christophe Copéret,[†] Jean Thivolle-Cazat,[†] Sudhakar Chakka,[‡] and Jean-Marie Basset^{*,†}

Laboratoire de Chimie Organométallique de Surface, UMR CNRS, ESCPE UCB 5265, 43 blvd du 11 Novembre 1918, F-69616 Villeurbanne Cedex, France, and BP Products North America Inc., 150 West Warrenville Road, Naperville, Illinois 60563

Received February 3, 2008; E-mail: basset@cpe.fr

Although the proven and potential deposits of natural gas are enormous, a majority of these exist in remote areas of the world. Methane, which is the main component of natural gas, represents an important reserve of fossil carbon but contributes much more than CO_2 to the global warming on earth. Transformation of remote natural gas into easily transportable higher hydrocarbons remains an important economical target and a huge scientific challenge.^{1,2} Conversion of methane to syngas³ followed by its transformation to heavier hydrocarbons by Fischer–Tropsch synthesis⁴ is rather well-established but requires high temperatures for the first step leading to limited overall yield,⁵ in addition requiring very high capital costs. The direct non-oxidative coupling of methane (NOCM) into ethane and hydrogen shows a large positive Gibbs free energy, affording very limited equilibrium conversions (Figure S1).⁶ Various attempts to accomplish the NOCM reaction used classical and ill-defined heterogeneous catalysts, either via a multistep process, (i) methane dissociation on Ru particles by chemisorption (and stepwise surface carbon–carbon bond formation) and (ii) liberation of products by hydrogenation, or via a single-step process with a Pt/sulfated zirconia catalyst.^{6–8} Another approach, called the oxidative coupling of methane (OCM), consists of using O_2 to increase the yield of the coupling reaction of methane into C_2 products. However, the global yield remained limited to <25% despite extensive efforts over two decades due to the gas phase free radical character of this reaction, hence the formation of large amounts of carbon oxides.^{9–11}

Silica-supported tantalum hydride $(\equiv\text{SiO})_2\text{Ta}-\text{H}$, **1**¹² (in equilibrium under hydrogen with $(\equiv\text{SiO})_2\text{Ta}(\text{H})_3$),¹³ is known to catalyze the total hydrogenolysis of light alkanes, including the hydrogenolysis of ethane¹⁴ into methane, in contrast to the silica-supported zirconium hydrides which do not cleave ethane.¹⁴ In an attempt to upgrade methane into ethane or higher hydrocarbons, it was interesting to consider the possibility of exploiting the microscopic reversibility of ethane hydrogenolysis reaction,¹⁴ that is, the coupling of methane into ethane and hydrogen. Despite the severe thermodynamic limitations (vide supra), we report here the first example of the selective catalytic coupling of methane into ethane and hydrogen, which occurs on the single-site catalyst $(\equiv\text{SiO})_2\text{Ta}-\text{H}$, **1** (eq 1):



The silica-supported tantalum hydride **1** was prepared by treatment under H_2 at 250 °C of the surface complexes

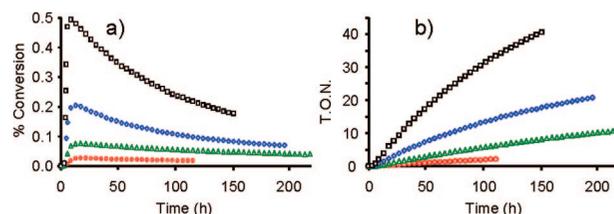


Figure 1. Non-oxidative coupling reaction of methane catalyzed by the silica-supported tantalum hydride $(\equiv\text{SiO})_2\text{Ta}-\text{H}$, **1**, at various temperatures: (a) conversion; (b) turnover (TON); \circ 250 °C; \triangle 300 °C; \diamond 375 °C; \square 475 °C.

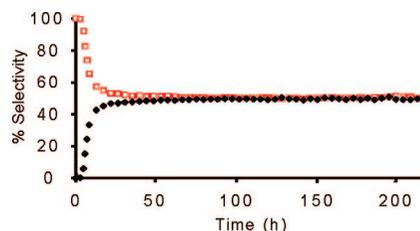


Figure 2. Selectivity obtained at 300 °C in the non-oxidative coupling reaction of methane catalyzed by the silica-supported tantalum hydride $(\equiv\text{SiO})_2\text{Ta}-\text{H}$, **1**: \square hydrogen; \diamond ethane.

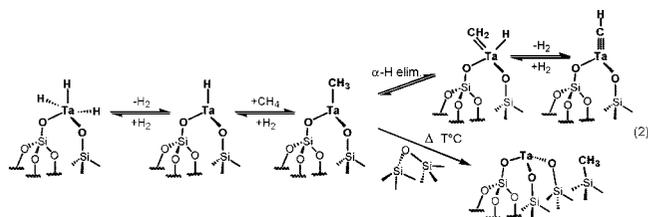
$(\equiv\text{SiO})_x\text{Ta}(\equiv\text{CHtBu})(\text{CH}_2\text{tBu})_{3-x}$, **2a** and **2b** (**a**: $x = 1$ or **b**: $x = 2$),¹⁶ resulting from the grafting of $\text{Ta}(\equiv\text{CHtBu})(\text{CH}_2\text{tBu})_3$, **3**¹⁷ on silica (Degussa, 200 m^2/g) previously dehydroxylated at 500 °C; at that temperature of reduction, about 30% of $(\equiv\text{SiO})_2\text{Ta}-\text{H}$ was already transformed into $(\equiv\text{SiO})_3\text{Ta}$ and $(\equiv\text{Si}-\text{H})$.¹⁸ When methane was contacted with **1** (5.35 wt % Ta) in a continuous flow reactor ($P_{\text{CH}_4} = 50$ bar, $T = 250$ to 475 °C, at a weight hourly space velocity WHSV = 0.44 h^{-1}), throughout the temperature range of 250 to 375 °C, ethane was formed selectively (>98% among hydrocarbons) along with an equimolar amount of H_2 . At the beginning, the conversion rate went through a maximum up to the thermodynamic ceiling, which is temperature-dependent (Figure S1), before reaching a pseudo steady state (Figure 1a), affording a cumulative turnover number, TON, of up to 40 after 147 h at 475 °C (Figure 1b). Kinetics is increased because high pressure of methane inhibits the reverse reaction of hydrogen with ethane. At 475 °C, besides trace amounts of propane, olefins (mainly ethylene) were observed, and their amount increased at lower contact time.

There was an initiation during which hydrogen was the main product (100%), and then the selectivities of hydrogen and ethane reached 50% each (Figures 2 and S2). At higher temperatures (e.g., 475 °C), the selectivity of hydrogen was higher than that of ethane due to dehydrogenation processes into olefins (mainly ethylene) (Figure S3).

[†] Laboratoire de Chimie Organométallique de Surface.

[‡] BP Products North America Inc.

The cumulative amount of H₂ evolved during the initiation period corresponded to 1.45 and 1.33 equiv per Ta at 250 and 375 °C, respectively. The hydrogen evolution arose from (i) its liberation from some remaining tris-hydride species,¹³ (ii) the C–H bond activation of methane, leading to surface tantalum–methyl species, and (iii) partial dehydrogenation processes into tantalum(V) carbene hydride and tantalum(V) carbyne¹³ (eq 2):



Indeed, such a process was evidenced by NMR spectroscopy of **1** on MCM-41 supports treated with ¹³CH₄ at 250 °C. In particular, peaks around 180 and 300 ppm, respectively, assigned to carbene and carbyne species, were observed (Figure S4).¹³ Moreover, it was also found that Ta–Me could transfer the methyl to silicon to produce ca. 30% of (≡SiO)₃Ta(III) and ≡Si–Me.

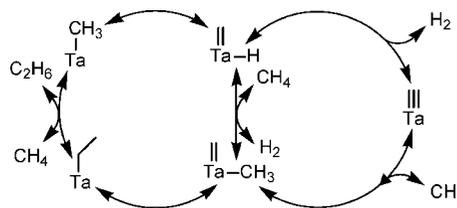
This process of stepwise C–H bond activation and dehydrogenation of Ta–Me to Ta(H)=CH₂ and Ta≡C–H was confirmed by the temperature-programmed reaction (TPRn) of methane (1 bar) carried out on (≡SiO)₂Ta–H between 25 and 375 °C (Figure S5). Two peaks of H₂ evolution (respectively, 0.66 equiv per Ta at 180 °C and 2.31 equiv per Ta at 375 °C) were consistent with the successive steps of C–H bond activation of methane (# 0.7 equiv of Ta), the progressive transformation of Ta–CH₃ to Ta≡CH and the catalytic formation of gaseous ethane by NOCM. TPRn experiment, carried out under 50 bar of methane (Figure S6), presented the same profile but with a shift of the two peaks by about 80 °C, consistent with an inhibiting effect of methane pressure on the carbyne species formation.

The reaction is then postulated to proceed first via a C–H bond activation of methane, leading to a surface tantalum–methyl species plus molecular hydrogen (eq 2). This tantalum–methyl undergoes dehydrogenation to a carbene–hydride and a carbyne (plus hydrogen) species. Both species are able to activate another molecule of methane by a σ -bond metathesis process,¹⁹ affording a methyl–methylidene key intermediate. Then, as shown for Cp*₂Ta(=CH₂)CH₃,²⁰ migratory insertion of the methyl group onto the carbene ligand would yield a tantalum–ethyl. Finally, the ethyl ligand can be displaced by methane in large excess via σ -bond metathesis, liberating ethane and leading back to a tantalum–methyl species. This mechanism is still speculative since the NMR spectra have been obtained at atmospheric pressure on a tantalum hydride supported on MCM-41, whereas the catalytic reaction has been performed on silica at 50 atm.

Noteworthy, previous works on the NOCM reaction involved only supported metal particles^{6–8,21–23} and often proceeded at relatively high temperatures in a two-stage process: methane dissociative chemisorption and products liberation under hydrogen, in order to bypass the severe thermodynamic limitations. However, the final yield relative to methane remains limited and the time necessary to switch from one stage to the other one is still too long for an industrial application.

In summary, we have shown the first example of the non-oxidative coupling reaction of methane into ethane and H₂,

Scheme 1. Proposed Mechanism for the Non-oxidative Coupling Reaction of Methane Catalyzed by the Silica-Supported Tantalum Hydride (≡SiO)₂Ta–H, **1**



catalyzed by a “single-site” catalyst, the silica-supported tantalum hydride (≡SiO)₂Ta–H, **1**. In the continuous flow reactor, at each temperature between 250 and 375 °C, the conversion at thermodynamic limitation was reached with a high selectivity (>98%) into ethane among hydrocarbon products. The reaction is likely to involve the tantalum–methyl–methylidene species as a key intermediate where the methyl ligand can migrate onto the tantalum–methylidene, affording the tantalum–ethyl. Such elementary steps are those frequently proposed in Fischer–Tropsch synthesis. The only difference between the two processes is that the CO dissociation step does not occur when starting from methane whereas it does with carbon monoxide.

Acknowledgment. This work was supported by BP Chemicals, the CNRS, and the ESCPE Lyon. The authors wish to thank B. Maunders and G. Sunley for fruitful discussions.

Supporting Information Available: Experimental details, Figures S1–S6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Lunsford, J. H. *Catal. Today* **2000**, *63*, 165–174.
- (2) (a) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987–1007. (b) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.
- (3) Choudhary, V. R.; Mondal, K. C.; Choudhary, T. V. *Energy & Fuels* **2006**, *20*, 1753–1756.
- (4) Van der Laan, G. P.; Beenackers, A. A. C. M. *Catal. Rev. Sci. Eng.* **1999**, *41*, 255–318.
- (5) *Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities*, NATO Science Series; Derouane, E. G.; Parmon, V.; Lemos, F.; Ribeiro, F. R., Eds.; Springer: Dordrecht, The Netherlands, 2005; Vol. 191, p 107.
- (6) Borko, L.; Guzzi, L. *Top. Catal.* **2006**, *39*, 35–43.
- (7) Pareja, P.; Mercy, M.; Gachon, J.-C.; Amariglio, A.; Amariglio, H. *Ind. Eng. Chem. Res.* **1999**, *38*, 1163–1165.
- (8) Kurosaka, T.; Matsuhashi, H.; Arata, K. *J. Catal.* **1998**, *179*, 28–35.
- (9) Liu, S.; Tan, X.; Li, K.; Hughes, R. *Catal. Rev. Sci. Eng.* **2001**, *43*, 147–198.
- (10) Labinger, J. A.; Ott, K. C. *J. Phys. Chem.* **1987**, *91*, 2682–2684.
- (11) Labinger, J. A. *Catal. Lett.* **1988**, *1*, 371–375.
- (12) Vidal, V.; Theolier, A.; Thivolle-Cazat, J.; Basset, J.-M.; Corker, J. *J. Am. Chem. Soc.* **1996**, *118*, 4595–4602.
- (13) Soignier, S.; Taoufik, M.; Le Roux, E.; Saggio, G.; Dablemont, C.; Baudouin, A.; Lefebvre, F.; De Mallmann, A.; Thivolle-Cazat, J.; Basset, J.-M.; Sunley, G.; Maunders, B. M. *Organometallics* **2006**, *25*, 1569–1577.
- (14) Chabanas, M.; Vidal, V.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M. *Angew. Chem., Int. Ed.* **2000**, *39*, 1962–1965.
- (15) Lécuyer, C.; Quignard, F.; Choplin, A.; Olivier, D.; Basset, J. M. *Angew. Chem., Int. Ed.* **1991**, *30*, 1660–1661.
- (16) Dufaud, V.; Nicolai, G. P.; Thivolle-Cazat, J.; Basset, J.-M. *J. Am. Chem. Soc.* **1995**, *117*, 4288–4294.
- (17) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370.
- (18) Saggio, G.; de Mallmann, A.; Maunders, B.; Taoufik, M.; Thivolle-Cazat, J.; Basset, J.-M. *Organometallics* **2002**, *21*, 5167–5171.
- (19) Bailey, B. C.; Fan, H.; Baum, E. W.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 16016–16017.
- (20) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21–39.
- (21) Belguéd, M.; Pareja, P.; Amariglio, A.; Amariglio, H. *Nature* **1991**, *352*, 789–790.
- (22) Koerts, T.; Van Santen, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1281–1283.
- (23) Koerts, T.; Van Santen, R. A. *Stud. Surf. Sci. Catal.* **1993**, *75*, 1065–1078.

JA800863X