Non-oxidative coupling of methane catalysed by supported tungsten hydride onto alumina and silica–alumina in classical and H_2 permeable membrane fixed-bed reactors†

K. C. Szeto,[a] S. Norsic,[a] L. Hardou,[a] E. Le Roux,[a] S. Chakka,[b] J. Thivolle-Cazat,[a]
A. Baudouin,[a] C. Papaioannou,[b] J.-M. Basset*[a] and M. Taoufik*[a]

Received 17th February 2010, Accepted 29th March 2010
First published as an Advance Article on the web 20th April 2010
DOI: 10.1039/c0cc00007h

Non-oxidative coupling of methane with high selectivity into ethane (>99% among hydrocarbon) in a classical fixed-bed reactor catalysed by SiO_2–Al_2O_3 or γ-Al_2O_3 supported tungsten hydride is presented. Continuous hydrogen separation, using a Pd–Ag membrane in a fixed-bed reactor, led to methane coupling far beyond the thermodynamic equilibrium conversion.

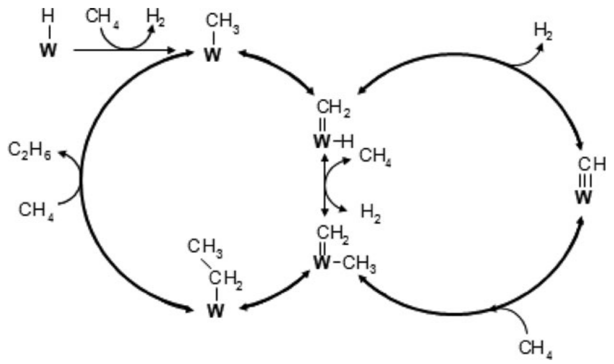
The utilisation of natural gas to produce petrochemical derivatives has become an important research field as a result of oil depletion. One the most abundant components in natural gas is methane. However, a large portion of methane is presently flared,[1] due to the lack of conventional methods to convert it into beneficial products.[2] Since gases emitted from CH_4 flaring are believed to contribute significantly to global warming and are under discussion for further restrictions, its conversion into valuable added products will most likely be an industrial key step in the future.[3] Currently, conversion of CH_4 usually involves several steps, in which at least one of them requires high temperature and often elevated pressure, that make the overall reaction highly energy consuming and expensive.[4–6] Thus, development of reaction pathways that convert CH_4 directly and selectively to added value products under mild conditions is greatly desired. An ideal reaction is the non-oxidative coupling of methane (NOCM) to form ethane and hydrogen (eqn (1)).

$$2CH_4 \rightleftharpoons C_2H_6 + H_2 \qquad (1)$$

Hydrogen is regarded as a clean energy carrier, in particular for vehicles,[7] and is in high demand. Ethane can easily be converted to heavy alkanes through metathesis reactions.[8,9] Moreover, ethane dehydrogenation into ethylene is central for polyethylene production.[10] Accounts reporting heavy hydrocarbon formation from CH_4 are predominantly based upon supported metal systems.[11–13] For instance Re and Mo supported on H-ZSM-5 convert CH_4 mainly to aromatics, with the selectivity to C_2H_6 being less than 7%.[14–16]

Recently, we reported exceptionally selective coupling of methane to hydrogen and ethane at moderate temperature in a simple fixed-bed reactor catalyzed by Ta-H supported on silica.[17] The proposed mechanism for this reaction involves tantalum-hydride-methylidene species as key intermediate.[17] On the other hand, an alternative system based on W–H on alumina or silica–alumina, which was developed in our laboratory, has shown improved activity in alkane metathesis compared to Ta–H on silica.[18,19] Moreover, this particular metal site is also active in unexpected reactions like direct conversion from ethene to propene and production of 2,3-dimethylbutane from isobutane.[20,21] Since metal-carbene-hydride seems to be an important intermediate in all these reactions,[18–23] systems based on tungsten hydride supported on SiO_2–Al_2O_3 or γ-Al_2O_3 (called W-H@support) have been investigated for NOCM. However, coupling of methane to hydrogen and ethane is thermodynamically unfavourable ($\Delta G \approx 17$ kJ mol^{-1} in the range of 25–500 °C) and thereby results in an extremely low equilibrium conversion (Fig. S1, ESI†).[11] To enhance the CH_4 conversion, a hydrogen selective membrane reactor can be used in order to shift the equilibrium in eqn (1) to the right hand side by constant removal of hydrogen.[24] Considerable research efforts have been devoted to the development of various membrane reactors based on separating/removing the products out of the reaction zone to improve the yield of desired product. Successful examples have been reported using Pd-based or ceramic proton conductor membranes to selectively remove H_2.[25–29]

We herein report the intriguing catalytic performance of tungsten hydride supported onto SiO_2–Al_2O_3 or γ-Al_2O_3 for NOCM using two types of fixed-bed reactor *i.e.* classical and equipped with a Pd–Ag membrane for H_2 removal.



Scheme 1 Proposed mechanism for the NOCM reaction catalysed by the W–H supported onto SiO_2–Al_2O_3 and γ-Al_2O_3.

---

[a] *Université Lyon 1, Institut de Chimie Lyon, CPE Lyon, CNRS, UMR 5265 C2P2, LCOMS, Bâtiment 308 F, 43 Blvd du 11 Novembre 1918, F-69616 Villeurbanne Cedex, France. E-mail: taoufik@cpe.fr, basset@cpe.fr; Fax: +33 (0)472431795; Tel: +33 (0)472431798*
[b] *BP, 150 W Warrenville Road, IL 60563, Naperville, USA*

† Electronic supplementary information (ESI) available: Experimental details, Fig. S1–S8 and Scheme S1. See DOI: 10.1039/c0cc00007h

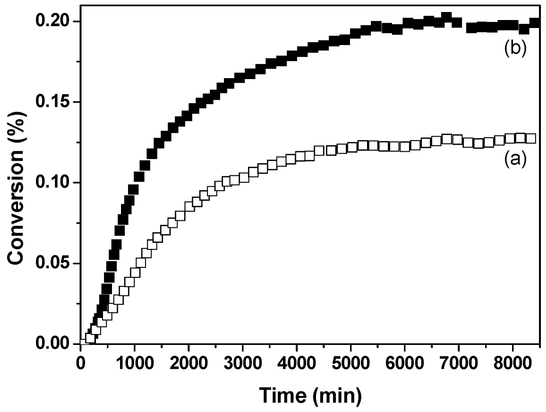


Fig. 1 Catalytic performances at 350 °C, 50 bar of (a) W-H@SiO_2–Al_2O_3 and (b) W-H@γ-Al_2O_3 for the NOCM in a classical fixed-bed reactor.

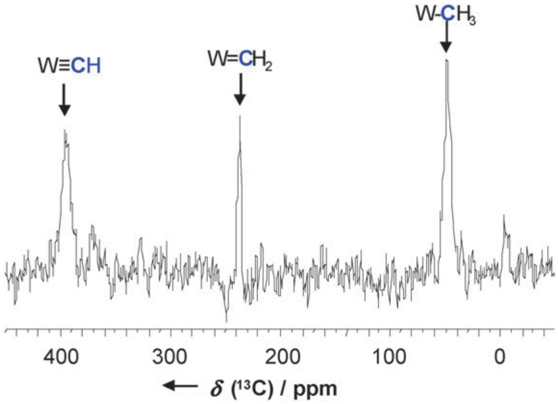


Fig. 2 ^{13}C CP MAS NMR spectrum of W-H@SiO_2–Al_2O_3 obtained after $^{13}CH_4$ activation at 150 °C.

W–H supported onto SiO_2–Al_2O_3 or γ-Al_2O_3 were prepared from the grafted W(≡C*t*-Bu)(CH_2*t*-Bu)$_3$ precursor under H_2 treatment at moderate temperatures as described elsewhere.[18,19]

When CH_4 is contacted with W–H@SiO_2–Al_2O_3 in a classical fixed-bed reactor, the conversion curve with respect to time on stream increases regularly to a stable plateau at 0.12% (Fig. 1a). Crucially, the activity remains constant after the initial state, giving the TON of 6 after 5800 min (about 4 days). Ethane is formed selectively (>99% among hydrocarbons) along with an equimolar amount of H_2 (Fig. S2a, ESI).† Importantly, no detectable traces of alkenes, alkynes, or aromatic compounds are found. When the maximum conversion is reached, a stable steady state is observed, showing an essential improvement compared to the Ta-H@SiO_2 which suffers from deactivation.[17]

Methane activation was monitored by IR spectroscopy and solid-state NMR in order to get an insight in the mechanism.[17] IR study shows that ν(W–H) bands decrease strongly after 5 h of reaction at 150 °C (≈80% consumption) and considered to be total after 24 h (Fig. S3, ESI).† After reaction of $^{13}CH_4$ onto W-H@SiO_2–Al_2O_3 at 150 °C for 24 h, the ^{13}C CP MAS NMR spectrum shows four distinct peaks at −4, 48, 237, and 395 ppm (Fig. 2). These peaks have chemical shifts compatible with tungsten methyl (48 ppm), methylidene (237 ppm), and methylidyne (395 ppm) ligands, respectively. These observations indicate that the methyl species formed after activation of CH_4 onto W-H@SiO_2–Al_2O_3, leads to a partial evolution of a mixture of unsaturated surface species, such as [W = CH_2] and [W≡CH], probably by subsequent α-H abstraction and α-H elimination, respectively (Scheme S1, ESI†).[17,30,31] The ^1H NMR spectrum is provided in the ESI (Fig. S4).† The signal at −4 ppm is attributed to methyl carbon attached to silicon ((Si–Me) or (Si(H)Me)) originated from the transfer of W–Me.[32] 2D ^1H-^{13}C HETCOR solid-state NMR spectra (Fig. S5, ESI)† confirms these attributions of the [W–Me] and [W = CH_2]. Similar observations have been also observed for the previously reported system based onto Ta-H@SiO_2.[17]

There is long initiation stage (300 min) where hydrogen is the only product. The cumulative amount of H_2 evolved during the initiation period corresponds to 2 H_2 per W (Fig. S6, ESI).† The hydrogen evolution can arise from two sources: (i) formation of tungsten monohydride by liberation of one H_2 per W from the presumed tungsten trihydride species, (ii) C–H bond activation of methane, releasing one H_2 per W and formation of tungsten methyl surface species (Scheme S1, ESI).† These results are consistent with the spectroscopic data and corroborate the postulated mechanism for NOCM postulated for Ta-H@SiO_2 surface species (Scheme 1).[17]

W-H@γ-Al_2O_3 was also tested in NOCM in a classical fixed-bed reactor to study the effect of the support on the activity under same conditions used for W-H@SiO_2–Al_2O_3. The conversion curve with respect to time on stream is described by a continuously increase to a stable plateau at 0.2% (Fig. 1b), which is notably higher than W-H@SiO_2–Al_2O_3 (Fig. 1a), and corresponds to the thermodynamic equilibrium. Importantly, the conversion remains constant under the equilibrium conditions, giving the TON of 11 after 5800 min, which is twofold as high as W-H@SiO_2–Al_2O_3. Ethane and H_2 are formed selectively in the same quantities, as shown in Fig. S2b (ESI),† followed by trace of propane (about 0.3%), originated from ethane metathesis.[33] No decrease in conversion or change in selectivity are observed after exposing the catalyst under the same conditions after 10 days (TON = 35, Fig. S7, ESI)† and thereby makes the W–H based system more active than the previously reported Ta–H system in the long run.[17]

Although the former approach offers a selective conversion of the usually inert CH_4 to added value products, thermodynamic limitations result in low yield. A known method to shift the equilibrium is to use a membrane reactor to remove selectively the formed product.[34] Conversion of CH_4 into C_2H_6 was then carried out exactly as in the classical reactor, apart from that a Pd–Ag-based H_2-permeable membrane reactor with a dynamic sweep-gas was used. Fig. 3a displays the conversion of the methane coupling reaction in a hydrogen selective membrane fixed-bed reactor loaded with W-H@γ-Al_2O_3. The conversion curve is completely different from what is observed in the classical fixed-bed reactor (Fig. 3b) and exhibits a higher initial activity (conversion = 0.6%) and maintains at a high level after 2500 min.

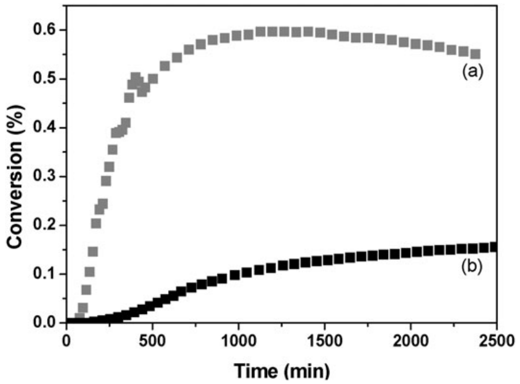


Fig. 3 Catalytic performances at 350 °C, 50 bar of W-H@γ-Al_2O_3 for the NOCM: (a) equipped with a Pd–Ag membrane and (b) classical fixed-bed reactor.

Constant removal of hydrogen accelerates the catalyst activation time to about 500 min (Fig. 3a) in comparison with the standard case of 5000 min (Fig. 1b). Then, the conversion slowly decreases. After 2500 min, the activity of W-H@γ-Al_2O_3 is 20 times higher in the membrane reactor (TON = 40) than in the classical reactor (TON = 2, Fig. S8, ESI).† Evaluation of the quantity of H_2 at both sides of the membrane indicates that 93% of it had been removed. There is a notable difference in the initiation step between the reaction performed in a classical fixed-bed reactor and the one equipped with a membrane. This can be explained by an equilibrium situation described in Scheme S1 (ESI).† Activation of methane in the first step involves elimination of hydrogen. Hence, removal of hydrogen favours the C–H activation of methane on W-H@γ-Al_2O_3.

In conclusion, alternative and stable catalysts based on W–H supported onto SiO_2–Al_2O_3 or γ-Al_2O_3 for the NOCM to ethane and hydrogen has been presented. It appears that CH_4 activation and conversion are further improved by the presence of a H_2 permeable membrane that constantly removes H_2 and thereby driving the NOCM reaction forward.

The authors thank BP for funding this work, *REB Research & Consulting* for providing the fixed-bed reactor equipped with a Pd–Ag membrane and helpful discussions.

Notes and references

1 J. Johnson, *Chem. Eng. News*, 2007, **85**, 10.
2 R. G. Bergman, *Nature*, 2007, **446**, 391–393.
3 C. D. Elvidge, E. H. Erwin, K. E. Baugh, B. T. Tuttle, A. T. Howard, D. W. Pack and C. Milesi, *Oil Gas J.*, 2007, **105**, 50.
4 M. Belgued, P. Pareja, A. Amariglio and H. Amariglio, *Nature*, 1991, **352**, 789–790.
5 T. Koerts and R. A. van Santen, *J. Chem. Soc., Chem. Commun.*, 1991, 1281–1283.
6 T. Koerts, R. A. van Santen, J. R. H. Ross, F. Solymosi, M. M. Bhasin, S. I. Woo, R. Vanhardeveld, D. Wang, A. Machocki, K. Foger, J. G. Goodwin and A. Sarkany, *Stud. Surf. Sci. Catal.*, 1993, **75**, 1065–1078.
7 L. Schlapbach and A. Zuttel, *Nature*, 2001, **414**, 353–358.
8 O. Maury, L. Lefort, V. Vidal, J. Thivolle-Cazat and J. M. Basset, *Angew. Chem., Int. Ed.*, 1999, **38**, 1952–1955.
9 J.-M. Basset, S. Chakka, M. Taoufik and J. Thivolle-Cazat, BP Oil International Limited, UK, WO 2008152371, 2008.
10 A. Virnovskaia, E. Rytter and U. Olsbye, *Ind. Eng. Chem. Res.*, 2008, **47**, 7167–7177.
11 L. Borko and L. Guczi, *Top. Catal.*, 2006, **39**, 34–43.
12 P. Pareja, M. Mercy, J. C. Gachon, A. Amariglio and H. Amariglio, *Ind. Eng. Chem. Res.*, 1999, **38**, 1163–1165.
13 T. Kurosaka, H. Matsuhashi and K. Arata, *J. Catal.*, 1998, **179**, 28–35.
14 T. V. Choudhary, E. Aksoylu and D. W. Goodman, *Catal. Rev. Sci. Eng.*, 2003, **45**, 151–203.
15 X. H. Gu, J. Zhang, J. H. Dong and T. M. Nenoff, *Catal. Lett.*, 2005, **102**, 9–13.
16 T. Koerts, M. Deelen and R. A. van Santen, *J. Catal.*, 1992, **138**, 101–114.
17 D. Soulivong, S. Norsic, M. Taoufik, C. Copéret, J. Thivolle-Cazat, S. Chakka and J. M. Basset, *J. Am. Chem. Soc.*, 2008, **130**, 5044–5045.
18 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.
19 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.
20 M. Taoufik, E. Le Roux, J. Thivolle-Cazat and J. M. Basset, *Angew. Chem., Int. Ed.*, 2007, **46**, 7202–7205.
21 N. Merle, F. Stoffelbach, M. Taoufik, E. Le Roux, J. Thivolle-Cazat and J. M. Basset, *Chem. Commun.*, 2009, 2523–2525.
22 M. Taoufik, E. Schwab, M. Schultz, D. Vanoppen, M. Walter, J. Thivolle-Cazat and J. M. Basset, *Chem. Commun.*, 2004, 1434–1435.
23 D. Soulivong, C. Copéret, J. Thivolle-Cazat, J. M. Basset, B. M. Maunders, R. B. A. Pardy and G. J. Sunley, *Angew. Chem., Int. Ed.*, 2004, **43**, 5366–5369.
24 L. S. Wang, K. Murata, A. Sayari, B. Grandjean and M. Inaba, *Chem. Commun.*, 2001, 1952–1953.
25 V. Hollein, M. Thornton, P. Quicker and R. Dittmeyer, *Catal. Today*, 2001, **67**, 33–42.
26 G. Marigliano, G. Barbieri and E. Drioli, *Chem. Eng. Process.*, 2003, **42**, 231–236.
27 W. H. Lin and H. F. Chang, *Catal. Today*, 2004, **97**, 181–188.
28 P. H. Chiang, D. Eng and M. Stoukides, *J. Electrochem. Soc.*, 1991, **138**, L11–L12.
29 P. H. Chiang, D. Eng, H. Alqahtany and M. Stoukides, *Solid State Ionics*, 1992, **53**, 135–141.
30 R. R. Schrock, K. Y. Shih, D. A. Dobbs and W. M. Davis, *J. Am. Chem. Soc.*, 1995, **117**, 6609–6610.
31 R. R. Schrock, S. W. Seidel, N. C. MoschZanetti, D. A. Dobbs, K. Y. Shih and W. M. Davis, *Organometallics*, 1997, **16**, 5195–5208.
32 S. Soignier, M. Taoufik, E. Le Roux, G. Saggio, C. Dablemont, A. Baudouin, F. Lefebvre, A. de Mallmann, J. Thivolle-Cazat, J. M. Basset, G. Sunley and B. M. Maunders, *Organometallics*, 2006, **25**, 1569–1577.
33 J. M. Basset, C. Copéret, D. Soulivong, M. Taoufik and J. Thivolle-Cazat, *Acc. Chem. Res.*, 2010, **43**, 323–334.
34 G. Saracco, H. Neomagus, G. F. Versteeg and W. P. M. van Swaaij, *Chem. Eng. Sci.*, 1999, **54**, 1997–2017.