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COMMUNICATION

High selectivity production of propylene from 2-butene: non-degenerate pathways to convert symmetric olefins *via* olefin metathesis†

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The first example of propylene production from 2-butene in promising yield is described by reacting *trans*-2-butene over tungsten hydrides precursor W–H/Al$_2$O$_3$ at 150 °C and different pressures in a continuous flow reactor. The tungsten carbene-hydride active site operates as a "bi-functional catalyst" through the disfavoured 2-butene isomerisation on W-hydride and 2-butenes/1-butene cross-metathesis on W-carbene.

Propylene supply has been a concern in the recent years. Classically, propylene is derived as a side product of petroleum cracking processes.[1] However, increased demand of polypropylene and propylene oxide is driving the development of on-purpose methods for production of propylene like olefin metathesis.[2,3] The cross metathesis reaction between ethylene and 2-butenes[4–6] to form propylene is an alternative method currently undergoing significant industrial development.

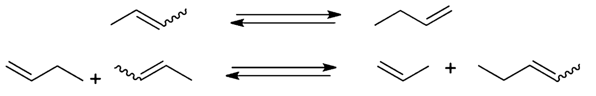
Olefin metathesis opens up new industrial processes for the production of important olefins in the field of petrochemicals. In particular, the production of propylene *via* olefin metathesis reaction from 2-butenes feedstock (major isomer and available from steam cracker or refinery based C4 streams) has received considerable attention.[11] The direct conversion of 2-butenes is a new scientific challenge for producing a wide variety of more valuable products such as propylene. As for all symmetrical olefins, the reaction of 2-butenes with typical olefin metathesis catalysts always leads, to the best of our knowledge, to degenerate products.[12] It is essential to develop a simple catalytic system capable of driving non-degenerate pathways to convert 2-butene to propylene in high yield.

Recently, we discovered a new and efficient catalytic reaction which transforms ethylene directly to propylene with a selectivity higher than 95%. This reaction is catalyzed by tungsten tris-hydrides supported on γ-alumina, which proceeds as a "tri-functional single site" catalyst.[7–9] However, the former system suffers from catalyst deactivation, leading to low yield of propylene.[8] Recently, we described another way to produce propylene from 1-butene. The mechanism of this reaction proceeds firstly by the thermodynamically favourable isomerisation of 1-butene to 2-butenes followed by cross-metathesis between 1-butene and the newly formed 2-butenes.[10]

A tungsten carbene-hydride W(H)(=CHR) has been postulated as the active site during the ethylene to propylene reaction, in which the tungsten-hydride performs dimerisation–isomerisation, and the tungsten-carbene moiety is responsible for the olefin metathesis.[8]

Herein, we report an efficient heterogeneous catalytic system to produce propylene from *trans*-2-butene according to Scheme 1, a feed which classically gives degenerate products in olefin metathesis. This reaction is catalysed by a "bifunctional single site" catalyst that proceeds in two steps: (i) *trans*-2-butene double bond migration to 1-butene by a tungsten hydride moiety, and (ii) cross-metathesis between 1-butene and 2-butenes on the tungsten carbene site to finally form propylene.

The precursor, tungsten hydride (WH$_3$/Al$_2$O$_{3\text{-}(500)}$),[7] was obtained by grafting of W($\equiv$CC(CH$_3$)$_3$)(CH$_2$C(CH$_3$)$_3$)$_3$,[13] on γ-alumina$_{(500)}$ (Johnson Matthey, 200 m^2 g^{-1}) followed by treatment under H$_2$ at 150 °C (see ESI†). Catalytic performance of *trans*-2-butene conversion was carried out in a continuous flow reactor (P_{C4H8} = 1 bar or 20 bar, T = 150 °C, flow rate = 20 mL min^{-1} or VHSV = 5200 h^{-1}). The reaction undergoes a steep maximal conversion rate of 4.9 mol$_{C4H8}$ mol$_W$$^{-1}$ min^{-1} at the start of reaction before reaching a pseudo plateau of 2.2 mol$_{C4H8}$ mol$_W$$^{-1}$ min^{-1}, yielding an overall turnover number, TON, of 14 500 after 90 h (Fig. 1a). In contrast to the results obtained in the direct transformation of ethylene to propylene (TON = 300 after 20 h),[8] the conversion profile in the beginning is quite linear with a deactivation rate of 0.12% h^{-1} (Fig. 1a). After this period, the conversion converged at 15%. WH$_3$/Al$_2$O$_{3\text{-}(500)}$ is known as an efficient classical olefin metathesis catalyst,[8] but it presents a surprisingly high activity in



Scheme 1 Reaction occurring during the conversion of 2-butene.

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† Electronic supplementary information (ESI) available: Additional reaction schemes, conversion and selectivity curves for the experiments carried out at 20 bar and mixtures of 1-butene and *trans*-2-butene as feed. See DOI: 10.1039/c2cc30172e

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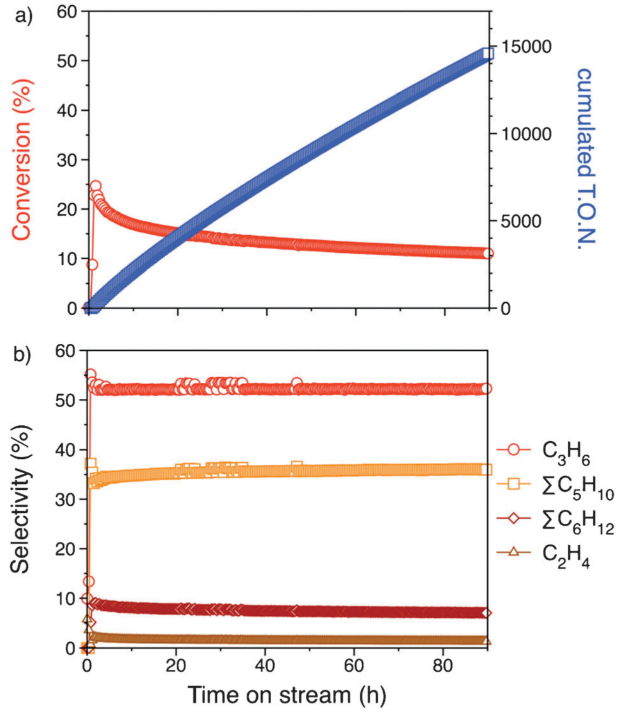


Fig. 1 (a) Conversion of 2-butene and cumulative TON *vs.* time on stream; (b) selectivity *vs.* time on stream obtained during the 2-butene conversion catalyzed by $WH_3/Al_2O_{3\text{-}(500)}$ (5.5 wt% W).

conversion of a symmetric olefin such as *trans*-2-butene, which classically only gives degenerate products.[11] This unprecedented reaction leads to an outstanding and fairly constant selectivity of 55% to propylene (Fig. 1b), giving a maximum productivity of 50.5 $\text{mmol}_{C_3H_6}\ \text{g}_{cata}^{-1}\ \text{h}^{-1}$ after 1 h on stream. Even after 20 h on stream, propylene is still the major product with 52.5% selectivity (productivity of 21.3 $\text{mmol}_{C_3H_6}\ \text{g}_{cata}^{-1}\ \text{h}^{-1}$). The other products of the reaction are *n*-pentenes at 36.5%, but only 9.5% selectivity to *n*-hexenes, and 1.5% of ethylene are observed at 20 h on stream (Fig. 1b). The excess of propylene *vs.* *n*-pentenes and the deficit of ethylene *vs.* hexenes can be explained by the cross metathesis between 2-butenes and ethylene. Therefore, as this reaction gives 2 mol of propylene per mole of ethylene (Scheme S1, ESI†), it explains the 16% difference in selectivity to propylene and 2-pentenes due to the consumption of 8% of ethylene.

Increasing the pressure to 20 bar while keeping the other parameters constant shows a beneficial impact on the conversion rate, which rises from 25% to 35% at the beginning of the curve (Fig. S1, ESI†). At 35 h on stream the cumulative TON reaches 10 000 at 20 bar *versus* 6000 at atmospheric pressure (Fig. S2, ESI†). In contrast to what was described for 1-butene conversion,[10] the drop of selectivity in propylene is small; it remains the major product, decreasing from 52% to 50%. This change in selectivity is in favour of pentenes, in which the selectivity slightly increases from 36.5% to 44% (Fig. 2). Increasing the pressure afforded a higher propylene productivity, as after 2 h on stream at 20 bar, the productivity rate is 64.8 $\text{mmol}_{C_3H_6}\ \text{g}_{cata}^{-1}\ \text{h}^{-1}$ and significantly higher than using 1-butene as feed (50.8 $\text{mmol}_{C_3H_6}\ \text{g}_{cata}^{-1}\ \text{h}^{-1}$).[10]

Furthermore, all linear butene isomers are detected in the gas phase. The isomeric distribution after 1000 min is 5% 1-butene, 73% *trans*-2-butene and 22% *cis*-2-butene, revealing the presence of unfavourable 2-butenes to 1-butene isomerisation reaction. As described in the case of 1-butene conversion to propylene,[10] the isomerisation of 2-butenes can occur on the W–H bond by the Cossee–Arlman mechanism[14,15] followed by a β-H-elimination. The reaction is equilibrium limited and disfavours the formation of 1-butene with a 1-butene : 2-butenes ratio of 5 : 95 at 150 °C and 1 bar.[16] This equilibrium is displaced by favourable cross-metathesis between 1-butene and 2-butenes, and thus drives the selectivity towards propylene.

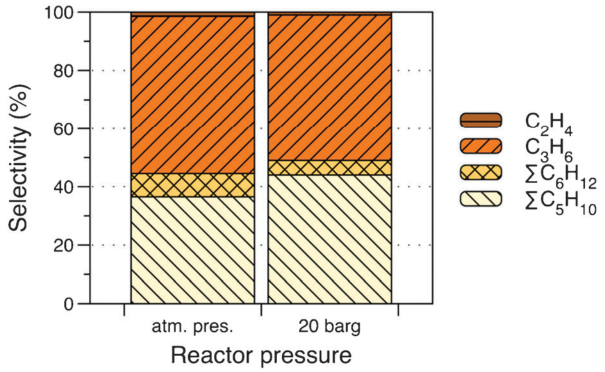
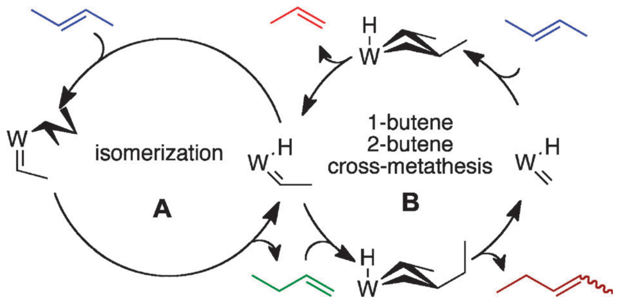


Fig. 2 Molar selectivity (%) in propylene at 20 h on stream for *trans*-2-butene conversion on $WH_3/Al_2O_{3\text{-}(500)}$ at 150 °C at 1 bar and 20 bar.

We believe that the relatively consistent selectivity to propylene at low and high pressure is indicative of 2-butenes cross-metathesis with 1-butene as the rate limiting step in the reaction pathway. As cross-metathesis is the slow step, probably due to the sterically unfavorable 1,2-disubstituted metallacyclobutane intermediate (Scheme 2), the forward and backward butenes isomerization set up the equilibrium concentration of 1-butene and 2-butene, which then sets the relative amounts of 1-butene/2-butene cross-metathesis and 1-butene self-metathesis. Increasing the pressure of the reaction to 20 bar increases the concentration of 2-butene, thereby increasing the rate of cross-metathesis while also favouring the primary cross-metathesis products propylene and pentenes. We note that analysis is somewhat complicated by the fact that isomerization of 1-butene back to 2-butenes is likely the fastest reaction occurring.[10]

Current data indicate that the concentration of 1-butene in the feed affects strongly the productivity of propylene. Hence, we also studied the effect of the proportion of 1-butene from 0%, 33%, 50%, 66% to 100% in 2-*trans*-butene feed on propylene production in a continuous flow reactor (P_{C4H8} = 1 bar, T = 150 °C, flow rate total = 20 mL min^{-1} or VHSV = 5200 h^{-1}).



Scheme 2 Catalytic cycle for the conversion of 1-butene on $WH_3/Al_2O_{3\text{-}(500)}$.

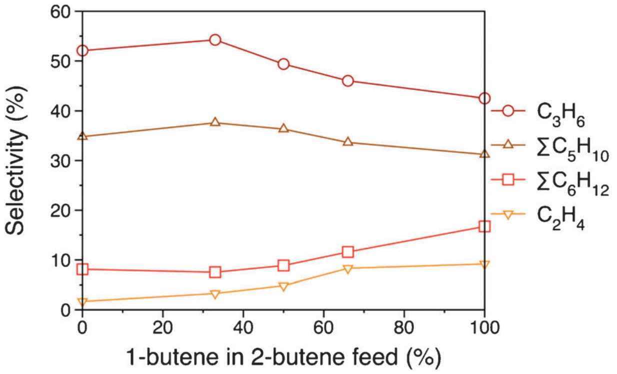


Fig. 3 Selectivity at 20 h on stream for 1-butene/2-butene metathesis catalyzed by $WH_3/Al_2O_{3\text{-}(500)}$ (5.5 wt% W) at 150 °C *vs.* 1-butene molar percentage in the 2-butene feed.

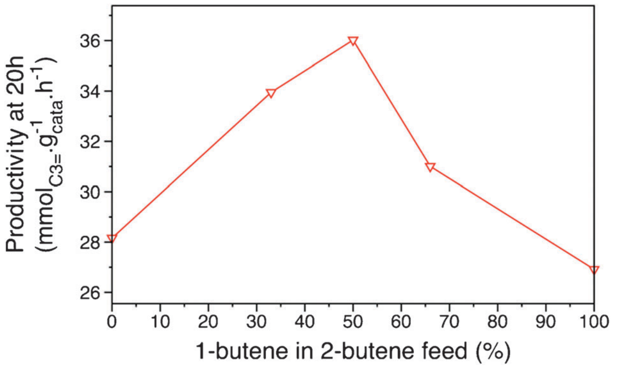


Fig. 4 Productivity of propylene at 20 h on stream for 1-butene/2-butene metathesis catalyzed by $WH_3/Al_2O_{3\text{-}(500)}$ (5.5 wt% W) at 150 °C *vs.* 1-butene molar percentage in the 2-butene feed.

For each ratio 2-butene/1-butene, the conversion profile is very similar, with a maximum conversion for the experiment where the feed is only composed of 1-butene. It is also notable that this experiment shows the fastest deactivation rate. After 20 h on stream, the 50% mixture gives a conversion rate with 3.8 $\mathrm{mol_{C4H8}\ mol_W^{-1}\ min^{-1}}$ (Fig. S3, ESI†). As expected, the selectivity in propylene is slightly better when 1-butene is a minor component of the feed. It decreases when the molar percentage of 1-butene increases, raising the selectivity in hexenes and ethylene, produced by self-metathesis of 1-butene. Operating with 33% of 1-butene in the feed gives the best selectivity in propylene with 55% at the steady state (Fig. 3).

At 20 h on stream the productivity rates span from 26.9 to 36.0 $\mathrm{mmol_{C3H6}\ g_{cata}^{-1}\ h^{-1}}$. The maximum productivity is reached with a 1 : 1 ratio of 1-butene to *trans*-2-butene (Fig. 4).

These results highlight the importance of the dual functionality of the supported tungsten carbene-hydride W(H)(=CHR) active site in the direct conversion of 2-*trans*-butene into propylene. A catalytic cycle that involves all these reactions, *i.e.* isomerisation of 2-butenes to 1-butene (cycle A), 1-butene/2-butenes cross metathesis (cycle B), can be proposed (Scheme 2).

A classical process for producing propylene[17] using olefin metathesis comprises three separate steps: (i) dimerising ethylene to 1-butene; (ii) isomerising 1-butene to 2-butenes; and (iii) cross-metathesis of 2-butenes by ethylene. The present reaction produces propylene directly in one single step *via* a non-degenerate pathway from 2-butenes that has important scientific, economical and technical advantages.[18]

In summary, the $WH_3/Al_2O_{3\text{-}(500)}$ system is the best unprecedented single-site catalyst precursor for the direct transformation of *trans*-2-butene to propylene, regarding either activity or selectivity; it operates as a "bi-functional single active site" tungsten carbene-hydride catalyst, opening up the non-degenerate pathway *via* 2-butene isomerisation to 1-butene and 2-butenes/1-butene cross-metathesis. This example simultaneously provides a novel process to utilise 2-butene feedstock to produce propylene in promising productivity.

Notes and references

1 J. S. Plotkin, *Catal. Today*, 2005, **106**, 10–14.
2 J. C. Mol, *J. Mol. Catal. A: Chem.*, 2004, **213**, 39–45.
3 A. H. Tullo, *Chem. Eng. News*, 2003, **81**, 15–16.
4 J. Engelhardt, *J. Mol. Catal.*, 1980, **8**, 119–125.
5 P. Amigues, Y. Chauvin, D. Commereuc, C. T. Hong, C. C. Lai and Y. H. Liu, *J. Mol. Catal.*, 1991, **65**, 39–50.
6 S. M. Pillai, G. L. Tembe and M. Ravindranathan, *Appl. Catal., A*, 1992, **81**, 273–278.
7 E. Le Roux, M. Taoufik, C. Coperet, A. de Mallmann, J. Thivolle-Cazat, J. M. Basset, B. M. Maunders and G. J. Sunley, *Angew. Chem., Int. Ed.*, 2005, **44**, 6755–6758.
8 M. Taoufik, E. Le Roux, J. Thivolle-Cazat and J. M. Basset, *Angew. Chem., Int. Ed.*, 2007, **46**, 7202–7205.
9 J. M. Basset, C. Copéret, D. Soulivong, M. Taoufik and J. Thivolle-Cazat, *Acc. Chem. Res.*, 2010, **43**, 323–334.
10 E. Mazoyer, K. C. Szeto, S. Norsic, A. Garron, J. M. Basset, C. Nicholas and M. Taoufik, *ACS Catal.*, 2011, **1**, 1643–1646.
11 X. Zehui, G. Chaoran and W. Peilin, *Prog. Chem.*, 2009, **21**(04), 784–790.
12 W. H. Meyer, M. M. D. Radebe, D. W. Serfontein, U. Ramdhani, M. du Toit and C. P. Nicolaides, *Appl. Catal., A*, 2008, **340**, 236–241.
13 D. N. Clark and R. R. Schrock, *J. Am. Chem. Soc.*, 1978, **100**, 6774–6776.
14 E. J. Arlman and P. Cossee, *J. Catal.*, 1964, **3**, 99–104.
15 P. Cossee, *J. Catal.*, 1964, **3**, 80–88.
16 D. R. Stull, E. F. Westrum and G. C. Sinke, *The chemical thermodynamics of organic compounds*, Krieger, Malabar, 1987.
17 A. G. Bozzano and B. K. Glover, *US Pat.*, 7586018, 2009.
18 C. P. Nicholas, E. Mazoyer, M. Taoufik, J.-M. Basset and P. T. Barger, *US Pat. Appl. Publ.*, 245569, 2011.