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Production of Propylene from 1-Butene on Highly Active "Bi-Functional Single Active Site" Catalyst: Tungsten Carbene-Hydride Supported on Alumina

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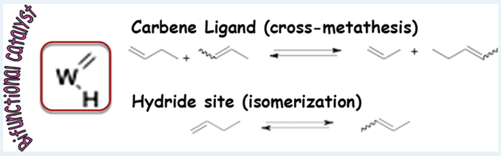
S *Supporting Information*

ABSTRACT: 1-Butene is transformed in a continuous flow reactor over tungsten hydrides precursor W—H/Al_2O_3, **1**, giving a promising yield into propylene at 150 °C and different pressures. Tungsten carbene-hydride single active site operates as a "bi-functional catalyst" through 1-butene isomerization on W-hydride and 1-butene/2-butenes cross-metathesis on W-carbene. This active moiety is generated in situ at the initiation steps by insertion of 1-butene on tungsten hydrides precursor W—H/Al_2O_3, **1** followed by α-H and β-H abstraction.



KEYWORDS: 1-butene, propylene, metathesis, supported tungsten, hydride, bifunctional

Propylene is a starting material for many important industrial processes. Classically, propylene is derived as a side product of petroleum cracking; however, increased consumption is driving the development of on-demand methods like olefin metathesis.[1,2] The cross-metathesis reaction between ethylene and 2-butenes[3−5] to form propylene is an alternative method currently undergoing significant industrial development.[1] 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 trishydrides supported on γ-alumina, **1**, which proceeds as a "tri-functional single site" catalyst, involving ethylene dimerization to 1-butene, isomerization of 1-butene to 2-butenes then cross metathesis between 2-butenes and ethylene leading to propylene.[6−8] However, the former system suffers from catalyst deactivation, leading to low yield of propylene.[7] We therefore wondered about using butenes containing feeds over this catalyst. Autometathesis of 1-butene yields ethylene and 3-hexenes, though in the presence of an acidic cocatalyst can afford propylene via the isomerization of 1-butene to 2-butenes followed by cross-metathesis of 1- and 2-butenes resulting in the formation of propylene and 2-pentenes.[9−11] In heterogeneous systems (like WO_3 supported on zeolite), the catalyst activity is generally quite low and small Volume Hourly Space Velocity (VHSV) value (typically <10 h^{-1}) is applied to obtain moderate conversion.[12]

Herein, we report an efficient heterogeneous catalytic system to selectively produce propylene from 1-butene. This reaction is catalyzed by tungsten carbene hydride supported on alumina, which functions as "bifunctional single site" catalyst that proceeds in two steps: (i) 1-butene isomerization to 2-butenes (tungsten hydride moiety), and (ii) cross-metathesis between 1-butene and 2-butenes (tungsten carbene site) to finally form propylene.

The precursor, tungsten hydride ($WH_3/Al_2O_{3\text{-}(500)}$) was obtained by grafting of $W(\equiv CC(CH_3)_3)(CH_2C(CH_3)_3)_3$[13] on a γ-alumina$_{(500)}$ (Johnson Matthey, 200 m^2 g^{-1}) followed by treatment under H_2 at 150 °C as described in the literature.[6] Catalytic performance of 1-butene conversion was carried out in a continuous flow reactor (P_{C4H8} = 1 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 7.2 $mol_{C4H8}\cdot mol_W{}^{-1}\cdot min^{-1}$ at the start of reaction before reaching a pseudo plateau of 3.4 $mol_{C4H8}\cdot mol_W{}^{-1}\cdot min^{-1}$, yielding an overall turnover number (TON) of 5450 after 22 h (Figure 1a). In contrast to the results obtained in the direct transformation of ethylene to propylene (TON = 300 after 22 h),[7] the conversion profile in the beginning is quite linear with a deactivation rate of 0.8% h^{-1} (Figure 1a). After this period, the conversion converged at 18%. As $WH_3/Al_2O_{3\text{-}(500)}$ is an efficient metathesis catalyst,[7,14] it might be assumed that the main products of the reaction are ethylene and 3-hexenes, originated from 1-butene self-metathesis. Surprisingly, an outstanding selectivity of 55% to propylene is observed (Figure 1b), giving a maximum productivity of 64.8 $mmol_{C3H6}\cdot g_{cata}{}^{-1}\cdot h^{-1}$ after 1 h on stream, which is 13 times faster than that observed with the system described by Liu et al.[10] Even after 22 h on stream, propylene is still the major product with 45% selectivity (productivity of 27.7 $mmol_{C3H6}\cdot g_{cata}{}^{-1}\cdot h^{-1}$). The other products of the reaction are n-pentenes, n-hexenes and

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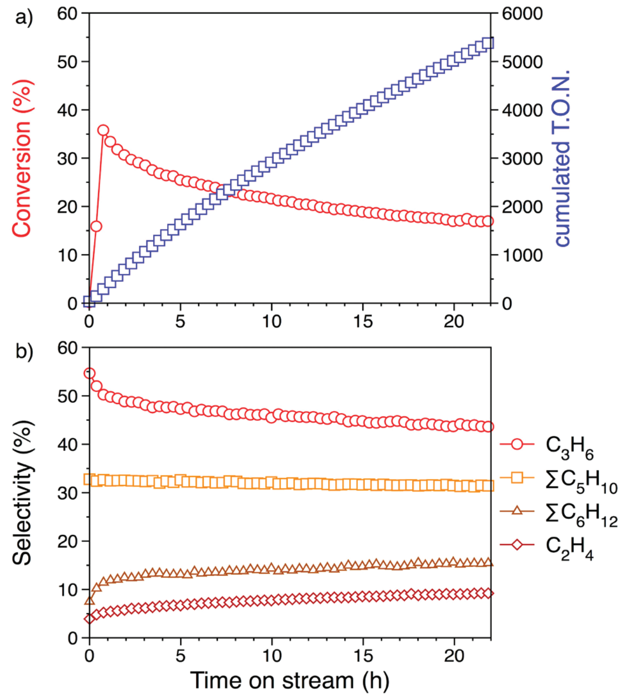
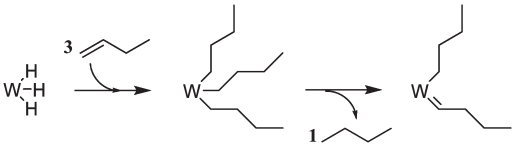


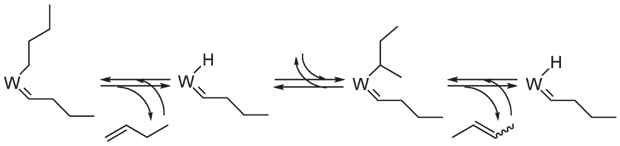
Figure 1. (a) Conversion and TON of 1-butene; (b) selectivities obtained during the 1-butene conversion catalyzed by $WH_3/Al_2O_{3\text{-}(500)}$, 1 (5.5 wt % W).

ethylene, with respectively 32%, 14%, and 9% selectivity at 22 h on stream (Figure 1b). It is reasonable to postulate that the initiation of the catalytic process occurs with a similar mechanism to that previously described for the direct conversion of ethylene to propylene:[7] in the first minutes on-stream, about 1 equiv of butane per grafted tungsten is formed (Supporting Information, Figure S1). It can be assumed that three 1-butene molecules insert into the tungsten trishydride precursor, affording a tungsten tris(n-butyl) species, $[W]((CH_2)_3CH_3)_3$. Then, n-butane is released by an α-H abstraction mechanism giving an n-butyl-n-butylidene species, $[W](=CH(CH_2)_2CH_3)((CH_2)_3CH_3)$ [eq 1].



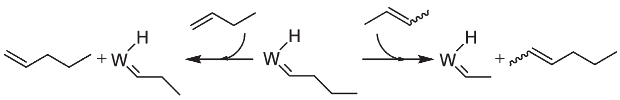
(1)

Subsequently, all linear butene isomers are detected in the gas phase. The isomeric distribution after 1000 min is 28% 1-butene, 61% trans-2-butene, and 11% *cis*-2-butene (Supporting Information, Figure S2), revealing a very fast isomerization of 1-butene to 2-butenes. Isomerization of 1-butene can occur either on the alumina support in an acid/base-catalyzed double bond migration[15] or by an insertion in the W−H bond, as described by the Cosse−Arlman mechanism[16,17] followed by a β-H-elimination. The reaction is equilibrium limited and favors the formation of 2-butenes with a 1-butene/2-butenes ratio of 25:75 at 150 °C and 1 bar.[18] We exposed $WH_3/Al_2O_{3\text{-}(500)}$ to dry O_2 to poison the W−H sites, as verified by the disappearance of ν(W−H) at 1930 cm^{-1}. No activity in 1-butene conversion on the poisoned catalyst was observed, confirming that tungsten hydride promotes the isomerization of 1-butene to 2-butenes [eq 2] as well as the cross-metathesis reaction.



(2)

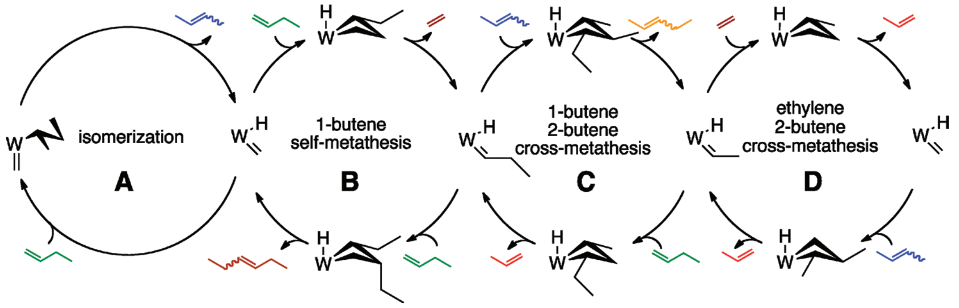
During the initiation of the metathesis reaction, the n-butylidene-hydride tungsten species can react with either 1-butene or 2-butenes to form respectively 1-pentene accompanied with tungsten propylidene-hydride center or 2-hexenes along with ethylidene-hydride tungsten species [eq 3].



(3)

These two newly formed carbenes undergo cross-metathesis to afford propylene and 2-pentenes from 1-butene and 2-butenes by following the classical Chauvin mechanism.[19] (Scheme 1, cycle C). If only the self-metathesis of 1-butene and 1-butene/2-butenes cross-metathesis take place, the relative proportion of 3-hexenes to ethylene and propylene to 2-pentenes should be 1:1. The excess of propylene versus 2-pentenes and the deficit of ethylene versus hexenes can be explained by the cross-metathesis between 2-butenes and ethylene produced by 1-butene self-metathesis. Therefore, as this reaction gives 2 mol of propylene per mol of ethylene (Supporting Information, Scheme S1), it explains the 12% difference in selectivity to propylene and 2-pentenes because of the consumption of 6% of ethylene. The trans/cis ratio of 2-pentenes produced is in favor of the trans isomer, 2.9:1 (Supporting Information, Figure S3), and superior to the thermodynamic ratio (1.5:1).[18] This result is explained by studying the relative stability of the possible metallacyclobutane intermediates (Supporting Information, Scheme S2). A similar tendency is observed for 3-hexenes. Increasing the pressure to 20 barg (bar, gauge-mode) while keeping the other parameters constant shows a beneficial impact on the conversion rate, which rises from 45% to 58% at the start of reaction (Supporting Information, Figure S4a). At 22 h on stream the cumulative TON reaches 9000 at 20 barg versus 5450 at atmospheric pressure. However, the selectivity to propylene drops in favor of hexenes (Supporting Information, Figure S4b). This result indicates that the increase of pressure favors the self-metathesis of 1-butene over the isomerization of 1-butene to 2-butenes. Given that the presence of 2-butenes is crucial for propylene production, we also studied the 1-butene/trans-2-butene cross-metathesis using a 1:1 mixture in a continuous flow reactor ($P_{\Sigma C4H8}$ = 1 bar, T = 150 °C, total flow rate =20 mL·min^{-1} or VHSV = 5200 h^{-1}). The reaction undergoes a steep maximal conversion rate of 7.2 $\mathrm{mol_{C4H8}\cdot mol_w{}^{-1}\cdot min^{-1}}$ at the start of reaction before reaching a pseudo plateau of 3.8 $\mathrm{mol_{C4H8}\cdot mol_w{}^{-1}\cdot min^{-1}}$, again with high selectivity to propylene of 55%, yielding an overall productivity rate at 20 h of 36.0 $\mathrm{mmol_{C3H6}\cdot g_{cata}{}^{-1}\cdot h^{-1}}$ (Figure 2a,b). Here, the conversion of butenes is quite constant with time. This result highlights the importance of the dual functionality of the active site and the rapid rate of isomerization under the studied conditions, since use of either 1-butene or mixed linear butenes yield the same approximate conversion and

Scheme 1. Catalytic Cycle for the Conversion of 1-Butene on $WH_3/Al_2O_{3\text{-}(500)}$



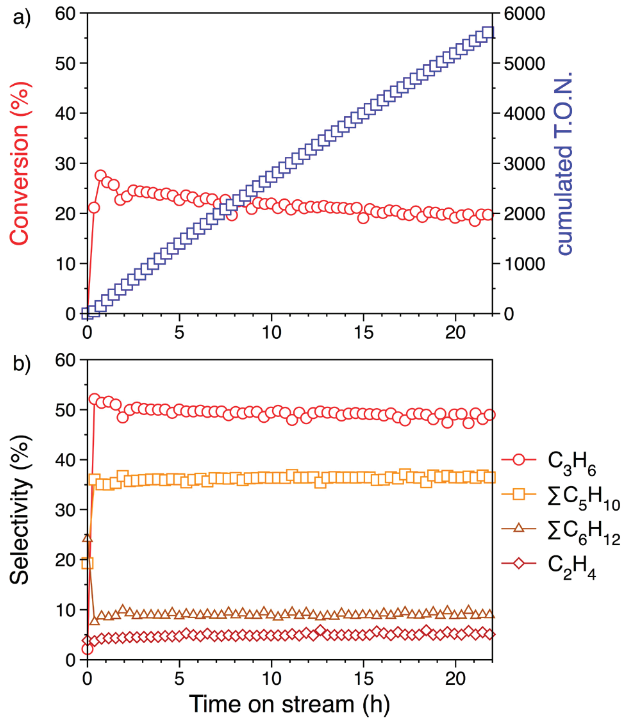


Figure 2. (a) Conversion and TON in 1-butene/2-butene cross-metathesis; (b) selectivities obtained during the 1-butene/2-butene cross-metathesis catalyzed by $WH_3/Al_2O_{3\text{-}(500)}$, 1.

selectivity. A catalytic cycle that involves all these reactions, that is, isomerization of 1-butene to 2-butenes (cycle A), 1-butene self-metathesis (cycle B), 1-butene/2-butenes cross-metathesis (cycle C) and ethylene/2-butenes cross-metathesis (cycle D), can be proposed (Scheme 1).

In contrast to reported examples of direct transformation of 1-butene to propylene in the literature,[9,10,12] the use of supported group 5[20] and group 6[6] monometallic carbene hydride sites to perform both isomerization and metathesis reactions leads to 100% selectivity to metathesis products and avoid at the same time the use of multiple catalyst systems as for typical industrial processes.[21−23]

In summary, the $WH/Al_2O_{3\text{-}(500)}$ system is the best single-site catalyst precursor for the direct transformation of 1-butene to propylene, regarding either activity or selectivity; it operates as a "bi-functional single active site" tungsten carbene-hydride catalyst through 1-butene isomerization and 1-butene/2-butenes cross-metathesis. We are currently studying further improvements of this system and employing the nature of butene isomerization on $WH_3/Al_2O_{3\text{-}(500)}$ to produce propylene directly from 2-butenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental section, additional curves displaying butene isomerization during the catalytic reaction, catalytic performance at 20 bar and extensive reaction schemes. This material is available free of charge via the Internet at http://pubs.acs.org.

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