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Study of ethylene/2-butene cross-metathesis over W-H/Al_2O_3 for propylene production: Effect of the temperature and reactant ratios on the productivity and deactivation

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ABSTRACT

A highly active and selective catalyst based on supported tungsten hydride for the cross-metathesis between ethylene and 2-butenes yielding propylene has been investigated at low pressure with various temperatures and feed ratios. At low temperature (120 °C), the catalyst deactivates notably with time on stream. This phenomenon was extensively examined by DRIFTS, TGA, DSC, and solid-state NMR techniques. It was found that a large amount of carbonaceous species were formed due to a side-reaction such as olefin polymerization which took place simultaneously with the metathesis reaction. However, at 150 °C, the catalyst was stable with time and thereby gave a high productivity in propylene. Importantly, the slight increase in temperature clearly disfavored the side reaction. The ratio of ethylene to trans-2-butene was also studied, and surprisingly, the W-H/Al_2O_3 catalyst is stable and highly selective to propylene even at substoichiometric ethylene ratios.

1. Introduction

Propylene supply has been a concern in recent years, mostly owing to strong demand growth for polypropylene, propylene oxide, and acrylonitrile [1–4]. Traditionally, propylene is produced as a coproduct of steam or catalytic cracking. Much of the current propylene production is therefore not “on purpose,” but as a by-product of ethylene and gasoline production. This leads to difficulties in coupling propylene production capacity with its demand in the marketplace. Moreover, much of the additional steam cracking capacity built in the near future will be based on using ethane as a feedstock, which typically produces only ethylene as a final product [5]. Although some hydrocarbons heavier than ethylene are present, they are generally not produced in quantities sufficient to allow for their recovery in an economical manner. In view of the current high growth rate of propylene demand, this reduced quantity of co-produced propylene from steam cracking will only serve to accelerate the increase in propylene demand and its value in the marketplace. The increasing demand for propylene therefore requires new ways for its production. The petrochemical industry has reacted and technology developers have seen this potential supply gap as an opportunity and have developed several “on-purpose” propylene production technologies. These approaches include propane dehydrogenation [6–8], olefin metathesis [9–11], and methanol to olefins [12–14]. All of these routes have been or will soon be exploited commercially to varying degrees. Furthermore, there is an emphasis on the development of routes to “green” or “bio-propylene”. The challenge of developing alternative technologies has become difficult because commercial technologies such as steam cracking and catalytic dehydrogenation (UOP’s C3 Oleflex™ technology) are well established and continuously subject to incremental improvements.

The production of propylene via olefin metathesis reaction is an established method, having been in used in production for tens of years, with a WO_3/SiO_2 catalyst used most frequently [11]. In recent years, different attempts to upgrade C2 or C4 alkenes resources to propylene via metathesis and to improve the existing catalytic systems have been carried out [15–17]. Our laboratory has been working extensively to develop alternative methods to produce propylene by using alkene metathesis reactions [18–22]. In this context, we recently discovered a new catalytic reaction

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that transforms ethylene directly to propylene at low temperature and pressure (150 °C, 1 bar) with a selectivity higher than 95% [23]. However, the tungsten hydride on alumina catalyst used here suffers from catalyst deactivation with time on stream, leading to a low yield of propylene if run without continuous regeneration. Recent studies reveal that this same **$WH/Al_2O_{3\text{-}(500)}$** system is a stable and highly active catalyst in the formation of propylene from linear butenes at the same conditions (150 °C, 1 bar), but the selectivity to propylene is moderate (55%) [24,25]. As the **$WH/Al_2O_{3\text{-}(500)}$** catalyst system is active for both ethylene to propylene and butenes to propylene and cross-metathesis of ethylene and 2-butenes is a well-established reaction, we desired to investigate it in cross-metathesis and compare this catalyst system to other known catalysts (Scheme 1).

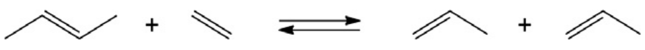
Multiple supported transition metal catalysts for alkene metathesis have been reported and the most successful are based on W, Mo, and Re. In particular, systems composed of highly loaded Re_2O_7 supported on alumina or silica–alumina show promising initial activity and selectivity even at room temperature [26,27]. These systems suffer from unknown deactivation processes. Conversely, supported tungsten oxide catalysts are less active for metathesis and generally require higher reaction temperatures and pressure (>350 °C and 10 bar) [28], but are notably less expensive and more robust than their rhenium and molybdenum counterparts [29,30]. The formation of propylene from ethylene and 2-butenes is generally accompanied by several by-products (pentenes, hexenes, heptenes) due to disproportionation reactions of C4 olefins: (a) 2-butenes isomerization to 1-butene; (b) 1-butene self-metathesis to form ethylene and 3-hexenes; (c) 1-butene and 2-butenes cross-metathesis to form propylene and 2-pentenes (Scheme 2). Optimal conditions to maximize the yield of propylene are achieved by adjusting the temperatures, pressures, and ethylene/2-butenes ratio to minimize the side reactions [31–33].

In general, these supported transition metal oxide catalysts have drawbacks such as unknown activation processes, significant deactivation processes (metal reduction, coking), or require severe reaction conditions (temperature and pressure) [34,35]. In an attempt to overcome the disadvantages of the classical olefin metathesis catalysts and to gain better molecular control over the catalyst active site, we prepared the **$WH_3/Al_2O_{3\text{-}(500)}$** system by the Surface Organometallic Chemistry (SOMC) method. Herein, we study the cross-metathesis between ethylene and trans-2-butene over **$WH_3/Al_2O_{3\text{-}(500)}$** to produce propylene at low temperature and pressure as observed in the selective direct conversion of ethylene or linear butenes to propylene. The performances of this catalyst have been evaluated in a continuous flow reactor at 1 bar using different temperatures and different reactant ratios in order to determine the optimal propylene productivity, affording (i) the best conversion rate, (ii) the highest selectivity in propylene, and (iii) the lowest deactivation rate seen for this catalyst system.

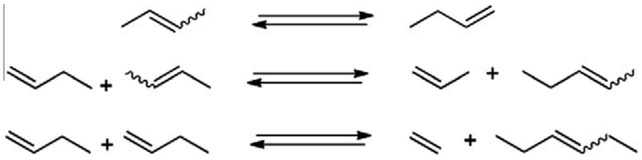
2. Materials and methods

2.1. Catalyst preparation

The catalyst (**$WH_3/Al_2O_{3\text{-}(500)}$**) was prepared according to published procedure reported elsewhere [36] and consisted of two steps. The first step involved grafting $W(\equiv CC(CH_3)_3)(CH_2C(CH_3)_3)_3$ [37] on γ-alumina at 66 °C under argon to obtain a well-defined $Al\text{-}O\text{-}W(\equiv CC(CH_3)_3)(CH_2C(CH_3)_3)_2$ fragment on the surface. The γ-alumina (Johnson Matthey, 200 $m^2\ g^{-1}$) was dehydroxylated at 500 °C prior to the grafting reaction. Excess molecular complex was washed off with dry pentane, and the solid was dried under high vacuum. The second step comprised a treatment of the latter solid under H_2 at 150 °C. The catalyst was then stored at −25 °C in the glovebox. Characterization of the catalyst is consistent with that described previously [36].



Scheme 1. Ethylene/trans-2-butene cross-metathesis.



Scheme 2. Side reactions in ethylene and 2-butenes cross-metathesis.

2.2. Characterization

Infrared spectra were recorded on a Nicolet FTIR 6700 spectrophotometer in diffuse reflectance mode, equipped with a MCT detector. Typically, 64 scans with a resolution of 4 cm^{-1} were applied for each spectrum. An air-tight cell with CaF_2 window was employed.

TGA experiments were performed in a Mettler Toledo TGA/DSC1 thermobalance. About 10 mg of the sample was placed in alumina crucible. The samples were heated from 35 °C to 800 °C at 20 °C min^{-1}. Air at a flow rate of 30 ml min^{-1} was used as the carrier gas. DSC analysis was performed in a Mettler Toledo DSC 1 instrument, equipped with an auto-sampler. The temperature and the heat flow of the equipment were calibrated with an indium standard. The sample was accurately weighed (around 10 mg) and heated from 40 °C to 160 °C at 10 °C min^{-1} with an empty aluminum pan as reference. Two successive heating and cooling cycles were performed, and only the second run was considered. Dry nitrogen with a flow rate set at 30 mL min^{-1} was used as the purge gas. The melting temperature (Tm) was measured at the top of the endothermic peak. The STARe thermal analysis software was used for the calculation.

^{13}C CP-MAS solid-state NMR spectra were collected on a Bruker NMR AVANCE 300 spectrometer. The sample was filled in a zirconia impeller of 4 mm and then transferred into the probe with a rotation speed of 10 kHz.

Elemental analysis was performed at the Central Analysis Service of the CNRS (Solaize, France) to determine the tungsten loading (found: 5.5 wt.% W).

2.3. Catalyst evaluation

Catalytic performance of trans-2-butene (99% provided by Scott) and ethylene (99.95% purchased from Air Liquide) conversion was carried out in a stainless steel continuous flow reactor ($P_{C4H8+C2H4}$ = 1 bar, T = 120–200 °C, total flow rate = 20 mL min^{-1} or VHSV = 5200 h^{-1}). The gases were purified with a column of molecular sieve and activated Cu_2O/Al_2O_3 and controlled by Brooks mass flow controllers. The catalyst was charged in the glovebox. A 4-way valve allowed isolation of the charged catalyst in the reactor from the environment and extensive purging of the tubes. The products were determined by an online HP 6890 GC equipped with 50 m KCl/Al_2O_3 column and FID.

3. Results and discussion

We first studied the cross-metathesis of ethylene/trans-2-butene (ratio 1:1) at different temperatures. At 120 °C, the reaction undergoes a steep maximal conversion rate of 6.6 $mol_{C4H8+C2H4}\ mol_W^{-1}\ min^{-1}$ at the start of reaction (1 h) before reaching a pseudo

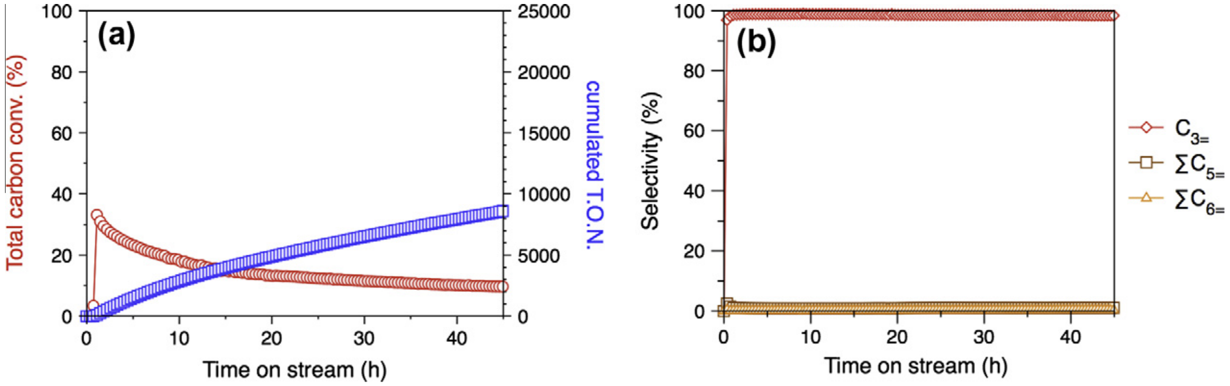


Fig. 1. (a) Total carbon conversion (○) and cumulated TON (□) *vs.* time on stream at 120 °C. (b) Product distribution.

plateau of 1.9 $\mathrm{mol_{C4=+C2=}\ mol_W^{-1}\ min^{-1}}$, yielding an overall turnover number, TON, of 9000 after 48 h (Fig. 1a). A very high selectivity in propylene of 98.7% is observed. The other products of the reaction are pentenes (1.1%) and hexenes (0.2%) (Fig. 1b). The propylene production rate for this reaction is thus 118.0 $\mathrm{mmol_{C3=}\ g_{cata}^{-1}\ h^{-1}}$ at maximum and 32.5 $\mathrm{mmol_{C3=}\ g_{cata}^{-1}\ h^{-1}}$ after 48 h on stream. In contrast to the results obtained in the direct transformation of ethylene to propylene (TON = 500 after 48 h) where the deactivation rate is quite high (7.5% $\mathrm{h^{-1}}$) [23], the catalyst in the beginning (until 10 h) undergoes a fast deactivation with a rate of 1.7% $\mathrm{h^{-1}}$ (Fig. 1a). At the end of the catalytic reaction, the deactivation is linear (0.23% $\mathrm{h^{-1}}$) and the recovered catalyst is agglomerated rather than as fine powder. Therefore, the catalyst used in the experiment has been studied after 48 h on stream by DRIFT, solid-state NMR, TGA, and DSC.

The DRIFT spectrum (Fig. 2) of the fresh catalyst exhibits bands at 3500–3800 $\mathrm{cm^{-1}}$, 2750–3000 $\mathrm{cm^{-1}}$, 1360–1465 $\mathrm{cm^{-1}}$ corresponding to $\nu_{(OH)}$ from alumina, $\nu_{(CH)}$ and $\delta_{(CH)}$ from residual hydrocarbon, respectively. Finally, the $\nu_{(WH)}$ band is presented at 1913 $\mathrm{cm^{-1}}$ [36].

The DRIFT spectrum of the used catalyst after 48 h on stream shows a complete disappearance of the $\nu_{(WH)}$ mode, indicating that all the W-H have been inserted by alkenes. Simultaneously, three intense bands centered at 2923, 2852 and 1465 $\mathrm{cm^{-1}}$, corresponding to typical $\nu_{(CH)}$ and $\delta_{(CH)}$ absorptions for long-chain alkyl groups were observed. This spectrum is similar to polyethylene obtained by polymerization of ethylene on supported metal hydrides [38]. The formation of long-chain alkyls is further confirmed by the solid-state NMR study (Fig. S1). A major peak at 32 ppm along with a shoulder around 30 ppm is observed, assigned respectively to amorphous and crystallized polyethylene [39]. Moreover, weak signals centered at 38, 20, and 14 ppm are detected, indicating the presence of a small degree of branched paraffin which is most likely due to incorporation of 2-butenes in the polymer [34,40]. The TGA profile of the used catalyst is presented in Fig. 3. It clearly indicates that carbonaceous species are formed at the surface of the catalyst during reaction. It is noteworthy that the amount of carbonaceous deposit is 35% of catalyst weight after the 48 h on stream.

DSC fusion profile (Fig. S2a) reveals that the species formed melt mostly at 129 °C which is similar to the fusion temperature of linear HDPE [41]. The crystallization profile (Fig. S2b) confirms the presence of mainly one type of carbonaceous deposit.

From this experiment, we see that propylene can be selectively formed over the **WH_3/Al_2O_3** catalyst system (98% selectivity) with high productivity by cross-metathesis of ethylene and trans-2-butene at 120 °C. The initiation and propagation steps of this reaction were elucidated by identifying the products formed while heating to the reaction temperature of 120 °C at 1 bar and 1:1 ratio ethylene/trans-2-butene. 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 [23]: in the beginning of the reaction, we noted that mainly ethane was released. It can be assumed that three ethylene molecules insert into the tungsten tris-hydride precursor, affording a tungsten tris(ethyl) species, $[W][(CH_2CH_5)_3]$. This selectivity can be explained by rapid ethylene insertion in the W-H bond, which is energetically more favorable rather than insertion of sterically hindered disubstituted olefins [42,43] (2-butenes), as described by the Cosse-Arlman mechanism [44,45]. Ethane formation is due to an α-H abstraction mechanism giving an ethyl-ethylidene species, $[W]({=}CHCH_3)((CH_2CH_3)$ (Scheme 3).

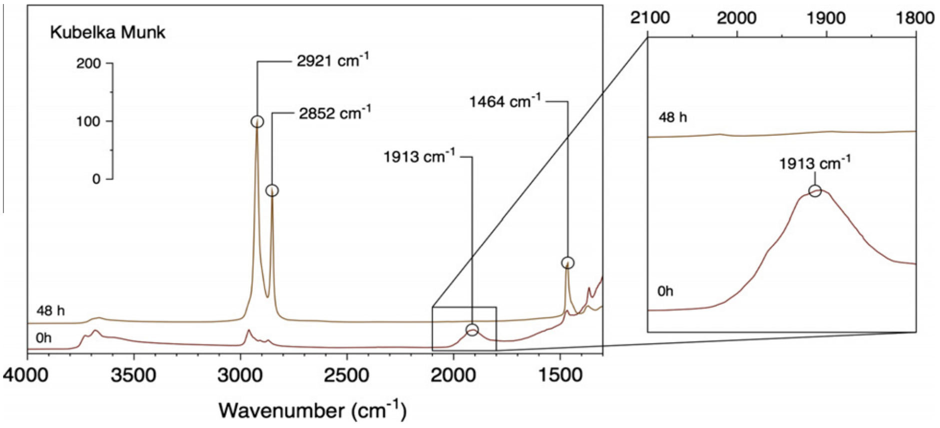


Fig. 2. DRIFT spectra of the fresh catalyst and used catalyst after 48 h on stream at 120 °C.

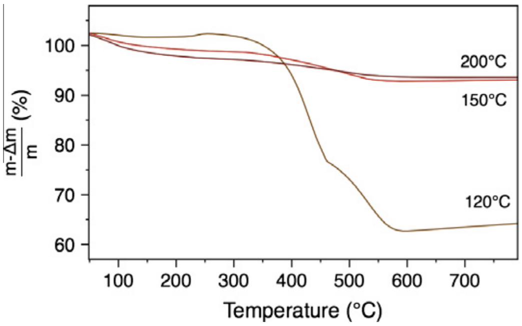
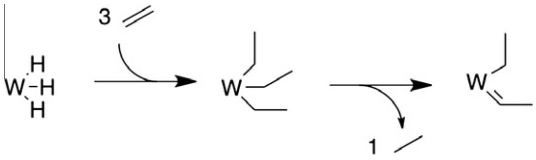
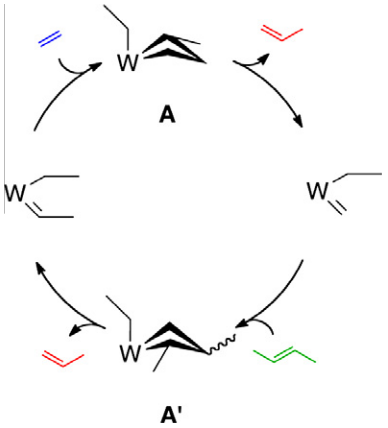


Fig. 3. TGA profile of the used catalyst after 48 h on stream at 120 °C, 150 °C, and 200 °C.



Scheme 3. Initialization step by ethylene insertion.



Scheme 4. Intermediates for the production of propylene from ethylene and trans-2-butene.

This newly formed carbene $[W]({=}CHCH_3)(CH_2CH_3)$ then undergoes metathesis reaction with ethylene to yield propylene and a new carbene, tungsten-methylidene-ethyl species $[W]({=}CH_2)(CH_2CH_3)$, following the classical Chauvin mechanism (**A**) [46]. The reaction of trans-2-butene with the tungsten methylidene-ethyl species gives a metallacyclobutene intermediate (**A′**) that by decomposition liberates propylene (Scheme 4).

Alternatively, the highly electrophilic tungsten alkyl-alkylidene species can undergo multiple insertions of ethylene at the tungsten σ-alkyl bond to finally result in polyethylene probably responsible for deactivation of the catalyst as described in the literature [34]. It is generally known that higher temperatures decrease catalyst activity in ethylene polymerization [40,47]. Hence, we studied the effect of the temperature on the stability of the catalyst during the cross-metathesis reaction between ethylene and trans-2-butene.

The reaction of $\mathbf{WH_3/Al_2O_{3\text{-}(500)}}$ with ethylene and trans-2-butene at 150 °C in the ratio 1:1 undergoes a steep maximal conversion rate of 7.4 $mol_{C4H8+C2H4}$ mol_W^{-1} min^{-1} at the start of reaction (1 h) before reaching a pseudo plateau of 5.4 $mol_{C4=+C2=}$ mol_W^{-1} min^{-1}, yielding an overall turnover number, TON, of 16000 after 48 h (Fig. 4a). In contrast to the results obtained at 120 °C (TON = 9000 after 48 h), the conversion profile in the beginning is quite linear with a negligible deactivation rate of only 0.03% h^{-1}. Similar selectivity to propylene (99%) is observed at 120 °C. Trace amounts of pentenes and hexenes are also detected (Fig. S3). The propylene production rate for this reaction is thus 133.4 $mmol_{C3=}$ g_{cata}^{-1} h^{-1} at maximum and 97.9 $mmol_{C3=}$ g_{cata}^{-1} h^{-1} after 48 h on stream. The used catalyst was also analyzed by TGA where no significant weight loss was observed (Fig. 3) confirming that deactivation by polymerization at 150 °C is negligible in accordance with the slow deactivation rate with respect to the same experiment carried out at 120 °C. This result shows that the polymerization by insertion of ethylene into the metal alkyl bond of the active tungsten alkyl-alkylidene species is disfavored at higher temperatures, as documented in the literature [40,47].

When the reaction is performed at 200 °C, the initial conversion rate (10.2 $mol_{C4=+C2=}$ mol_W^{-1} min^{-1}) is higher than that observed at 150 °C (Fig. 4) with a similar selectivity in propylene (99%, see Fig. S4) giving a high initial productivity of 180.9 $mmol_{C3=}$ g_{cata}^{-1} h^{-1}. However, the conversion profile undergoes a linear deactivation rate of 0.30% h^{-1} which is 10-fold greater than the 150 °C experiment giving an overall TON of 22000 with a propylene productivity of 98.5 $mmol_{C3=}$ g_{cata}^{-1} h^{-1} after 48 h on stream. Note that the selectivity to propylene at the different temperatures studied (120, 150, and 200 °C) is fairly consistent around 99%.

The TGA analysis performed on the used catalyst (Fig. 3) does not show a significant amount of carbonaceous species suggesting that the observed deactivation does not arise from an ethylene polymerization process as in the 120 °C experiment. We have previously shown that the highly oxophilic-supported metal species are unstable at high temperature ($\geqslant$ 150 °C) and consequently change their coordination spheres either by opening M—O—M bridges (M = Si, Al) [48] or by formation of unsaturated hydrocarbons bonded to the metal (cyclopentadienyl tuck-in complexes, carbyne) to give inactive species in the conversion of alkanes and olefins [49–51].

Our current experiments show that while propylene selectivity is relatively unaffected by reaction temperature, catalyst stability and propylene productivity are significantly affected by the reaction temperature. At 120 and 200 °C, the catalyst undergoes a notable deactivation though we have shown that 2 different mechanisms are likely responsible for the deactivation. On the other hand, at 150 °C, the $\mathbf{WH_3/Al_2O_3}$ catalyst system is extremely stable with time on stream. The overall turnover number achieved after 48 HOS increases as the reaction temperature increases, primarily due to the increased conversion level obtained in the metathesis portion of the reaction. This suggests that overall yield of propylene can be optimized through selection of reaction parameters as the TON at 150 °C will eventually be greater than that at 200 °C due to the lower deactivation rate.

Most importantly, excellent selectivity and productivity toward propylene can readily be obtained over $\mathbf{WH_3/Al_2O_3}$ as catalyst even at low temperature and 1:1 ratio of ethylene and trans-2-butene. Typically, an excess of ethylene is utilized [52] in addition to high temperature and elevated pressure in order to achieve high selectivity to propylene for classical supported catalysts based on tungsten oxide. Hence, the same experiment ($P_{C4H8+C2H4}$ = 1 bar, T = 150 °C, total flow rate = 20 mL min^{-1} or VHSV = 5200 h^{-1}) was performed by using the classical heterogeneous catalyst [53,54] based on tungsten oxide supported on silica (WO_3/SiO_2) synthesized and activated as shown by Lokhat, et al. No significant activity was observed. The present result shows that the $\mathbf{WH/Al_2O_{3\text{-}(500)}}$ catalyst is clearly more active and selective (99% in propylene) for ethylene/2-butene cross-metathesis than the classical catalyst WO_3/SiO_2 at low temperature and pressure. However, our working

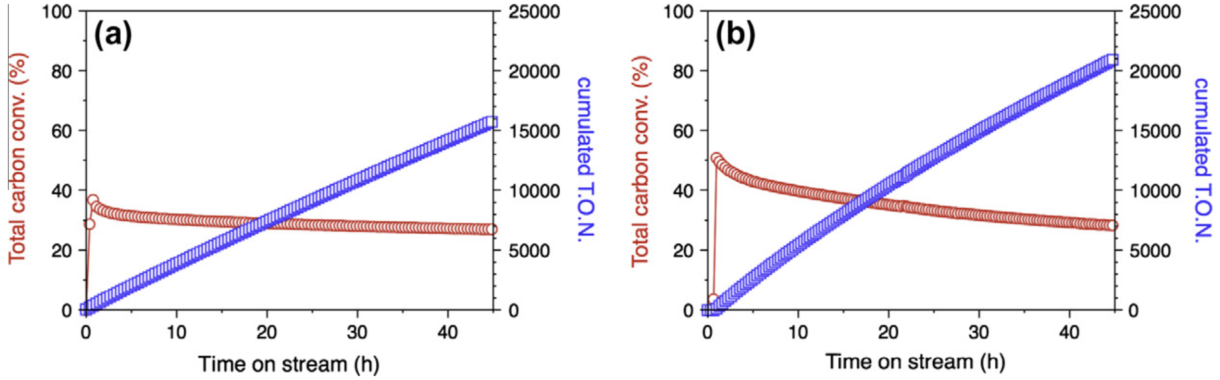


Fig. 4. Total carbon conversion (○) and cumulated TON (□) *vs.* time on stream for ethylene/trans-2-butene metathesis at (a) 150 °C and (b) 200 °C.

conditions (low temperature and pressure) are very different from the industrial conditions (350 °C, 35 bar).

Given the differences in reactivity and deactivation rates seen in conversion of ethylene to propylene [23] and 2-butene to propylene [24] as well as to obtain the maximum selectivity and productivity in propylene, the influence of the proportion of ethylene in the feed during the cross-metathesis reaction between ethylene and trans-2-butene catalyzed by **WH$_3$/Al$_2$O$_3$** was then studied to optimize the reaction conditions and its influence on deactivation rate. The study has been conducted at the same conditions ($P_{C4H8+C2H4}$ = 1 bar, T = 150 °C, total flow rate = 20 mL min^{-1} or VHSV = 5200 h^{-1}) by varying the proportion of ethylene from 0%, 10%, 18%, 35%, 45% to 70% mol in trans-2-butene feed.

The selectivity to propylene increases with the proportion of ethylene in the feed, starting from 55% when no ethylene was in the feed to 99% when 70% of ethylene was added (Fig. 5). The maximum propylene production rate during the cross-metathesis reaction is obtained when the reactor is fed with 35% of ethylene in the trans-2-butene, with 142.8 mmol$_{C3=}$ g$_{cata}$ h^{-1} (Fig. 6). The maximal conversion rates span from 5.0 to 9.2 mol$_{C4H8+C2H4}$ mol$_{W}^{-1}$ min^{-1}, whereas the deactivation rate is quite constant for all ratios: ca. 0.11% h^{-1}. (Fig. 7). At low ethylene content in the feed, notable amounts of pentenes are observed. These products originate from 2-butenes isomerization on tungsten-hydride moiety to 1-butene followed by cross-metathesis as highlighted in Scheme 2 [24].

A detailed analysis of the latter results shows that the addition of a small amount of ethylene (10%) to the trans-2-butene feed does not increase the overall conversion (Fig. 7), but does significantly improve the selectivity to propylene, increasing it from 55% to 79% (Fig. 5), thus implying that butenes to propylene is still the dominant reaction mechanism [24] but that ethylene coordinates strongly and gives cross-metathesis products when it enters the reaction cycle. Increasing the ethylene content to 18% slightly improves overall conversion and again significantly increases the propylene selectivity to 90%. With an ethylene content of 35%, the overall conversion level is the highest observed. Given these results, as the concentration of ethylene in the feed exceeds above 10%, ethylene/2-butene cross-metathesis becomes the dominant reaction. We are unable to rule out ethylene dimerization to 1-butene followed by isomerization to 2-butene, as in the ethylene to propylene mechanism, as a reaction pathway here. But, given that the overall conversion level and deactivation rate for cross-metathesis are consistent with the butenes to propylene data published previously [24,25] rather than ethylene to propylene data [23], and that the moles of ethylene converted (9.8 mmol h^{-1}) are consistent with the moles of propylene produced (19.5 mmol h^{-1}) according to the 2:1 mol ratio of the cross-metathesis reaction (Scheme 1), the extent of dimerization (pathway for direct conversion of ethylene to propylene) is limited under these conditions.

When the ethylene proportion in the feed exceeds 35%, the conversion rate and the productivity to propylene decrease even though the selectivity remains constant (>98%). At these higher ethylene content levels, the productivity of propylene is also higher than that of either the butenes to propylene [24,25] or ethylene to propylene [23] reaction showing that cross-metathesis of ethylene and 2-butenes is predominant. As previously noted, ethylene dimerization is the slowest reaction occurring in the system at 150 °C [23]. Additionally, we have previously shown that the concentration of 1-butene in the 2-butene feed affects both selectivity to propylene (as well as pentenes and hexenes) and productivity

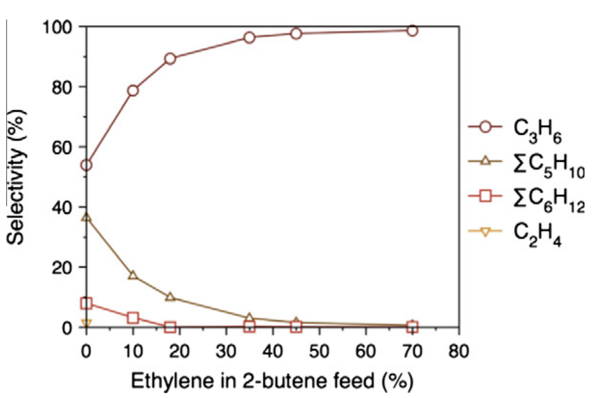


Fig. 5. Selectivity at 20 h on stream for ethylene/trans-2-butene metathesis on **WH/Al$_2$O$_{3\text{-}(500)}$** at 150 °C *vs.* ethylene molar percentage in the trans-2-butene feed.

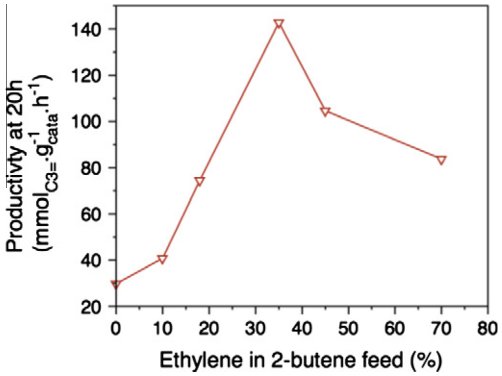


Fig. 6. Productivity in propylene at 20 h on stream for ethylene/trans-2-butene metathesis on **WH/Al$_2$O$_{3\text{-}(500)}$** at 150 °C *vs.* ethylene molar percentage in the trans-2-butene feed.

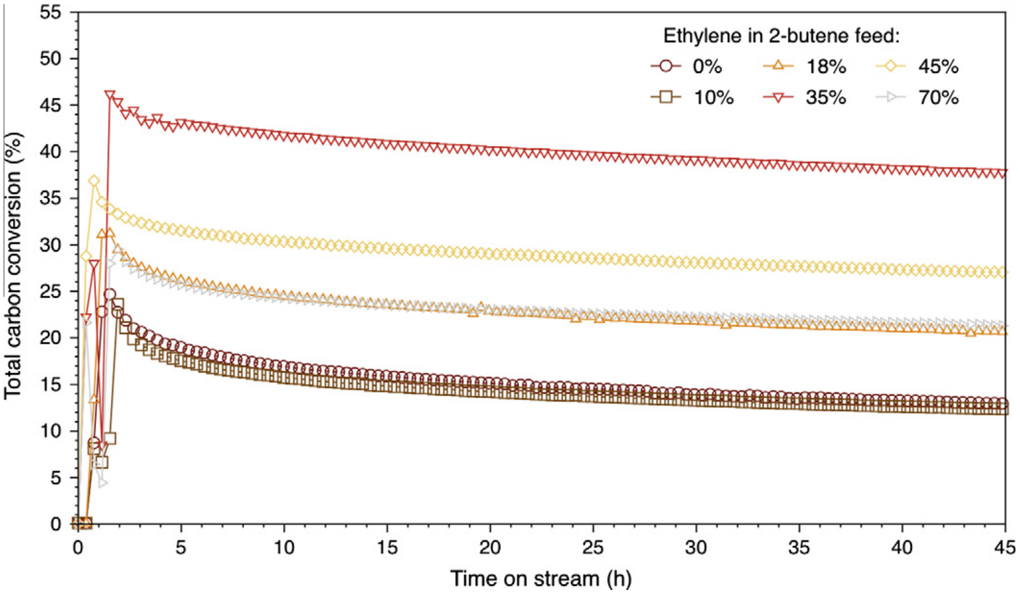


Fig. 7. Total carbon conversion *vs.* time on stream for ethylene/trans-2-butene metathesis on **$WH/Al_2O_{3\text{-}(500)}$** at 150 °C for different feed compositions 0%, 10%, 18%, 35%, 45%, and 70% mol. of ethylene in the 2-butene feed.

[24]; here, we do not observe a decreased selectivity to propylene nor an increase in heavy olefins, suggesting that the dimerization and isomerization reactions are limited.

The lowered propylene productivity at greater than 35% ethylene content in the feed is probably due to the stronger coordination of ethylene (smallest and most reactive of the alkenes) than 2-butenes on the active sites, thereby limiting the probability of the catalyst to undergo a productive cross-metathesis reaction to produce propylene. Degenerate metathesis pathways are not indicated in Scheme 4, but with a high concentration of ethylene in the feed, the probability of undergoing non-productive degenerate metathesis to continuously yield an ethylidene species is high. Even though the production of propylene from ethylene/2-butene cross-metathesis is a stoichiometric reaction, having a lower than stoichiometric ethylene to 2-butenes ratio allows for the highest productivity of propylene over the $W\text{-}H/Al_2O_3$ catalyst system because the relative rates of productive and non-productive metathesis are best matched.

4. Conclusion

Propylene can be obtained selectively and in high productivity by cross-metathesis between ethylene and 2-butenes catalyzed by **WH_3/Al_2O_3** prepared by the SOMC method. In contrast to the classical system (WO_3/SiO_2), the present catalyst yields exceptional productivity of propylene at low temperature and pressure. Unprecedentedly, the highest propylene productivity is obtained at less than stoichiometric ratios of ethylene in the trans-2-butene feed. The current system may have a remarkable economical and energetic impact since a lower amount of ethylene is required. The challenge we will pursue is to fully investigate the catalyst lifetime in an industrial context and the regeneration under hydrogen to recover the initial **WH_3/Al_2O_3** catalyst.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.01.016.

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