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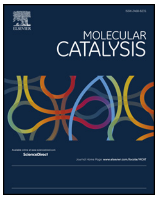

Tandem olefin isomerization/metathesis and volatiles capture: Accessing light olefin blends and broadening the scope to higher olefins

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ABSTRACT

The potential of a catalytic orthogonal tandem olefin isomerization/metathesis system combined with a “volatiles capture” approach was studied for the preparation of light olefins, using a model olefin substrate. Different isomerization-metathesis (pre-)catalyst combinations enabled the capture of up to 35 mol% of volatile olefins (C_3-C_6). This goes together with the possibility to tune the average molecular weight of the residual olefin fraction, which depends on the (pre-)catalysts combination.

1. Introduction

Olefins are among the most important *building blocks* in the chemical industry [1]. Light olefins (e.g. ethylene and propylene) are precursors for oligomers and polymers, while heavier olefins ($\geq C_{10}$) are precursors for surfactants, coatings, paints, varnishes, etc. Traditionally, light olefins are prepared by hydrocarbon-cracking (e.g. FCC process), or by alcohol dehydrogenation (although applied on a smaller scale). Alternatively, linear α-olefins can also be obtained via ethylene oligomerization or Fischer-Tropsch synthesis. As a strategy to transform C=C bonds, olefin metathesis is a highly versatile reaction and the development of robust single-site ruthenium alkylidene catalysts opened the route to tandem transformations of a broad range of substrates [2–4]. Within the context of tandem isomerization-metathesis reactions, the concurrent isomerization in ruthenium-catalyzed olefin metathesis has attracted interest, being either undesired or desired [5–12].

The olefin isomerization-metathesis combination is explored industrially as part of the *Shell Higher Olefins Process* - SHOP (Fig. 1a) [13]. Briefly, α-olefins are subjected to sequential steps of olefin isomerization and olefin metathesis, forming olefins in the C_{11} - C_{14} range. The transformation of this sequential approach into a similar tandem isomerization-metathesis process has been described for *trans*-3-hexene, using ruthenium-based isomerization and metathesis (pre-)catalysts. Both catalytic transformations occurred simultaneously and produced an equilibrium distribution of olefins ranging from C_3 to C_{17} (Fig. 1b) [14]. The substrate scope for this approach has been expanded to renewable substrates [15–19].

Due to the reversibility of the olefin metathesis reaction, some general strategies are employed to increase the conversion to the desired product. The driving forces for reaction completion include the use in excess of one of the reactants, strain relief, and, removal of a volatile (co-)product. For instance, the products 1,4-diene **1b** [20] and ^{18}O-labelled allylic alcohol **2b** [21] were distilled off (“volatiles capture”) from the corresponding RCM (ring- closing metathesis) reaction when using **1a** and **2a** as substrates, respectively (Fig. 2).

In the light of the number of applications of olefins, either lighter or heavier, this work explored the combination of tandem olefin isomerization-metathesis and “volatiles capture” strategies to obtain light olefins, using a model olefin (1-octene) substrate (Fig. 3). Because the distribution equilibrium obtained in a tandem isomerization-metathesis approach [14,15] is expected to re-establish while removing the volatile lower-molecular-weight olefins, the preparation of olefin blends with two distinct distribution profiles (lower- and higher-molecular-weight olefins) would be possible [22].

2. Experimental

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Toluene and 1-octene were distilled over sodium/benzophenone and stored over molecular sieves (4 Å) under argon. All complexes were used as received (second-generation Grubbs - **G2** and second-generation Hoveyda-Grubbs **HG2** metathesis (pre-)catalysts: Sigma-Aldrich; Umicore M_{42} (pre-)catalyst **UM42** and bromo (tri-*tert*-butylphosphine)palladium(I) dimer **PdBr**: Strem chemicals; chlorohydridocarbonyltris(triphenylphosphine)ruthenium(II) [23,24]

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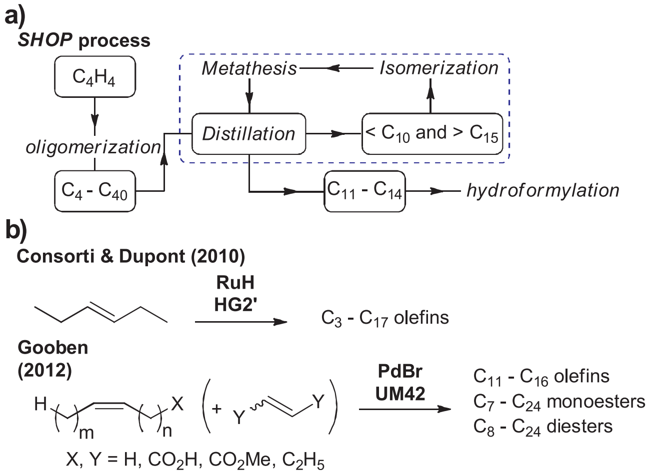

Fig. 1. Olefin isomerization and metathesis reactions in the preparation of olefin blends: a) sequential and b) in tandem (**RuH**: $RuClH(CO)(PPh_3)_3$; **PdBr**: $[PdBr(tBu_3P)]_2$; **HG2**’: ionic-tagged second-generation Hoveyda-Grubbs (pre-)catalyst).

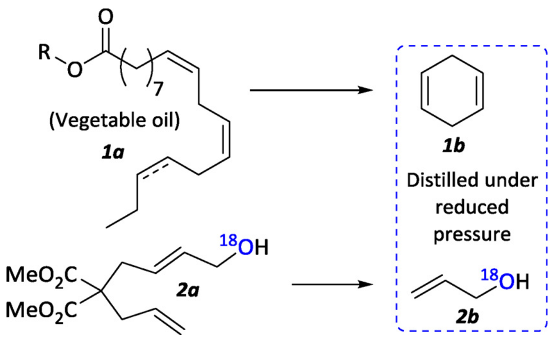

Fig. 2. “Volatiles capture” strategy applied in olefin metathesis.

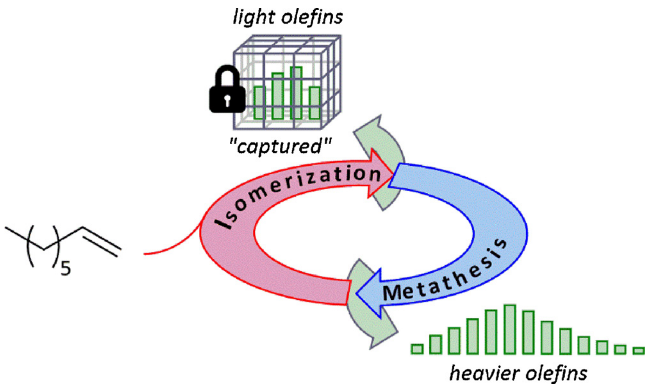

Fig. 3. Strategy explored in this work.

RuH: ABCR). Products were analyzed by GC (Master GC DANI) or GC–MS (Shimadzu GC-2010). More detailed information can be found in the Supporting Information.

2.1. Typical procedure for tandem isomerization-metathesis with “volatiles capture”

1-Octene : isomerization (pre-)catalyst : metathesis (pre-)catalyst = 1000 : 2 : 1. 1-Octene (1.0 mL, 6.4 mmol) and mesitylene (internal standard, 50 μL, 0.34 mmol) were diluted with 10 mL of toluene in a Schlenk tube (reaction flask) and connected to an inverted distillation equipment (see Supporting Information) containing a Schlenk tube immersed in ice/NaCl (temperature −10 to −5 °C) as collector flask. In the collector flask were added mesitylene (50 μL, 0.34 mmol, internal standard for GC) and 20 mL of toluene. In separate flasks, the isomerization (pre-)catalyst (12.8 μmol) and metathesis (pre-)catalyst (6.4 μmol) were dissolved in 5 mL of toluene, each. The solutions were then transferred to the flask containing 1-octene (already immersed in an oil bath at the studied temperature). At the end of the reaction, aliquots from both reaction and collector flasks were taken and analyzed immediately by GC or GC–MS.

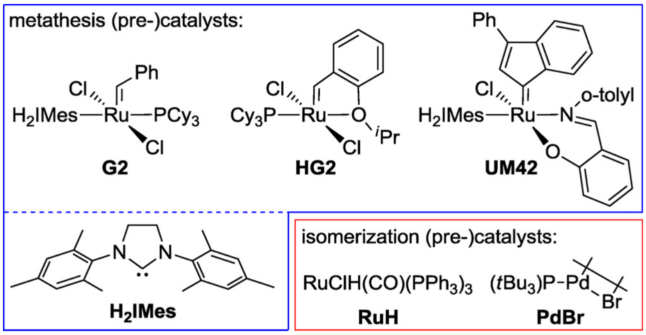

Fig. 4. Metathesis and isomerization (pre-)catalysts screened.

3. Results and discussion

The potential applicability of the volatiles capture strategy was first investigated in a system that enables the removal of the volatile olefins but without their capture [25]. These reactions were performed either at 50 or 100 °C, using 1-octene as substrate, **RuH** as isomerization (pre-)catalyst and **HG2** as metathesis (pre-)catalyst (Fig. 4). The effect of the removal of light olefins on the olefin distribution was evident. Compared to 50 °C, a lower absolute concentration of all olefins was observed in the equilibrium distribution at 100 °C (Fig. 5a). Nevertheless, the relative concentration of each olefin was little affected by the reaction temperature, showing only a small shift to higher-molecular-weight olefins at higher temperature (Fig. 5b). These results confirm the compatibility of the (pre-)catalysts **RuH** and **HG2** under the applied reaction conditions, allowing the continuous removal of lower-

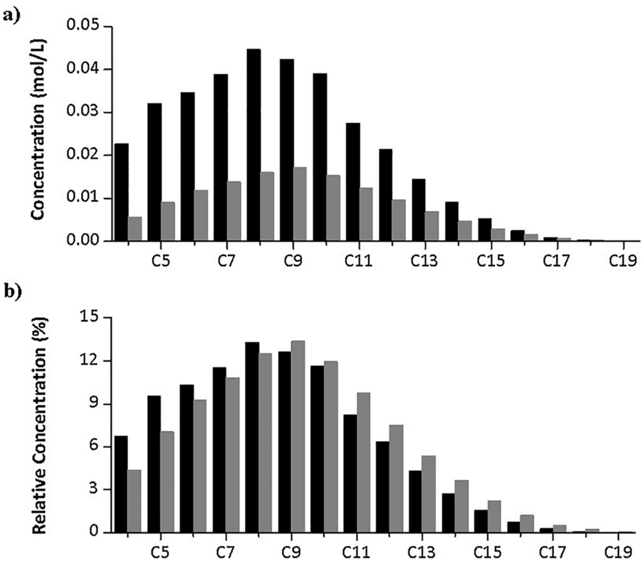

Fig. 5. Olefins distribution profiles for the tandem isomerization-metathesis of 1-octene in an open system without volatiles capture: a) absolute concentration (mol/L) and b) relative concentration. Reaction conditions: 1-octene (6.4 mmol, 1000 equiv.); **RuH** (12.8 μmol, 2.0 equiv.); **HG2** (6.4 μmol, 1.0 equiv.); 6 h; 50 °C (black bars) or 100 °C (gray bars).