

The metathesis of α -olefins over supported Re-catalysts in supercritical CO₂

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At 35 °C, in the presence of supercritical carbon dioxide (80–150 bar) as a solvent, α -olefins (RCH=CH₂, R = C₄–C₆) undergo highly selective self-metathesis catalyzed by supported Re-oxide (7%). To the best of our knowledge, this is the first procedure for the metathesis of alkenes, in which heterogeneous catalysts are combined with the use of dense CO₂. The intrinsic eco-compatibility and the unique physicochemical properties of this medium offer both environmental and synthetic advantages: not only conventional toxic solvents (*e.g.* *n*-heptane and toluene) can be replaced, but the reaction is faster. For instance, after 2 h, the average conversion of 1-octene is 67% and 40% in scCO₂ and *n*-heptane, respectively. The product of self-metathesis, 7-tetradecene, can be isolated in yields up to 68%. At 90 bar, the reaction is rather sensitive to the mole fraction of the olefin (in scCO₂); though, the enhancement of the pressure (and the density) of the supercritical medium does not induce significant effects on either the rate or the selectivity of the process. The nature of the catalytic support also greatly affects the reaction outcome: Re-oxide shows good activity if dispersed over γ -Al₂O₃, while silica-based systems are ineffective.

Introduction

The olefin metathesis reaction is a powerful, elegant, clean, and atom economical means of constructing complex carbon frameworks.¹ As such it has undergone tremendous development since its discovery in the 1950s,² culminating in the Nobel Prize in Chemistry awarded to Chauvin, Grubbs, and Schrock in 2005. The applications of the reaction span from petrochemistry (*e.g.* in the synthesis of linear higher olefins and of propene), to polymer chemistry (*e.g.* polynorbornene and poly(dicyclopentadiene) *via* ring-opening-metathesis polymerization), to fine chemistry. The metathesis of alkenes represents the archetype green chemistry reaction for clean syntheses with reduced emissions of hazardous wastes to the environment.³ In this context, the increasing demand for safer and more efficient synthetic procedures has spurred research towards new homogeneous catalysts able to operate under milder conditions, to improve the reaction selectivity, and to extend the synthetic scope of the metathetic process in general.⁴ Excellent examples were designed by Grubbs *et al.*,^{3–5} based on Ru- and Mo-carbene complexes capable of tolerating a variety of polar and protic groups for the ring-closing metathesis (RCM) of functionalized dienes to produce valuable cyclic intermediates.

Further improvements of the synthetic potential, scope, and eco-compatibility of the metathesis lie, in our opinion, in the use of alternative safer and *greener* solvents able to replace conventional media, typically hydrocarbons (hexane and toluene)

or light chlorinated compounds (dichloromethane and carbon tetrachloride).^{3,6} This is a largely unexplored area: only a few recent patents and papers report on the application of dense CO₂ or ionic liquids as solvents for RCM and ROMP (ring opening metathesis polymerization) processes,^{7,8} using either Grubbs catalysts or transition metal salts [RuCl₃, Ru(H₂O)₆(tos)₂, and WCl₆/Ph₄Sn].

Compressed CO₂ as a solvent is perfectly suited for metathesis applications, especially if combined with the use of heterogeneous catalysts. First of all its solvating power towards alkenes is high.⁹ Secondly, dense carbon dioxide is very efficient at penetrating meso- and micro-porous supports used for solid catalysts, thanks to its low viscosity (η) and high diffusivity (D) (0.01–0.03 mPa s and $\sim 0.07 \times 10^{-6}$ m² s⁻¹, respectively).¹⁰ In both its liquid and supercritical states, CO₂ as a solvent/carrier, can therefore improve the mass transfer (and the reaction rate) for a variety of different processes catalysed by solid materials. Examples are alkylations,^{8–11} etherifications and esterifications,¹² hydrogenations and hydroformylations,^{13,14} and oxidations¹⁵ carried out either in batch or in continuous-flow conditions, in the presence of zeolites, supported acids, metals on polysiloxane-based Deloxan or Amberlyst resins, on MCM solids, and on alumina and silica.

Yet, to the best of our knowledge, the combined use of heterogeneous catalysts and CO₂ solvent has not been investigated for the metathesis of olefins. This observation in conjunction with our long-standing interest for green synthetic methods using CO₂ and its derivatives,¹⁶ have inspired the present work. We report that in the presence of Re₂O₇ supported on γ -Al₂O₃, not only the self-metathesis of α -olefins occurs efficiently in supercritical carbon dioxide (scCO₂), but the reaction also takes place faster than in classic media (*n*-heptane and toluene). The properties of scCO₂ increase the overall efficiency and sustainability of the transformation.

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Results

Catalysts

The heterogeneous catalysts for the metathesis of olefins are usually transition metal oxides such as Re_2O_7 and MoO_3 supported on several inorganic matrices (SiO_2 , Al_2O_3 , ZrO_2 and TiO_2).^{1,17} The catalytic systems used in this study were based on Re_2O_7 supported on both $\gamma\text{-Al}_2\text{O}_3$ (from Puralox Condea and from Alfa-Aesar), and SiO_2 (from Aldrich). These were prepared by a conventional impregnation technique,¹⁸ using commercial ammonium perrhenate (NH_4ReO_4) as the precursor of the active phase. Each sample was calcined in dry air at 550 °C, and immediately before use, it was activated in dry N_2 at the same temperature (details in the Experimental section). Four different catalysts were obtained: three of them were supported on two different aluminas, while the fourth specimen was dispersed on SiO_2 . They were labelled as Re-A₁, Re-A₂, Re-A₃, and Re-S, respectively. The final metal content (by weight) was determined by optical ICP, and it ranged from 6.4 to 7.0%. The catalysts on $\gamma\text{-Al}_2\text{O}_3$ (Re-A₁, Re-A₂, and Re-A₃) were also characterised by TEM. Catalyst characteristics are listed in Table 1.

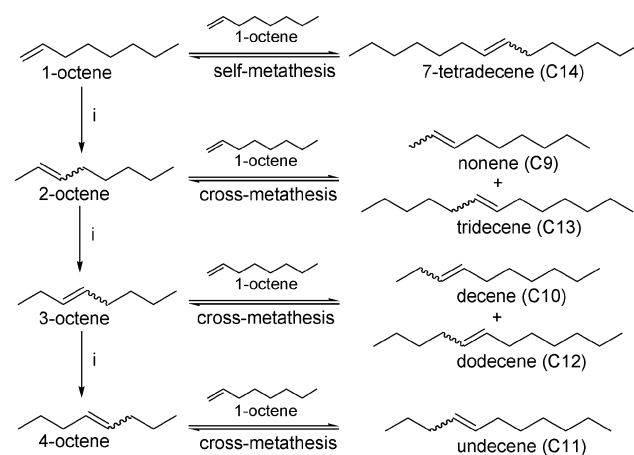
Self-metathesis of 1-octene in conventional solvents (method A) and in supercritical CO_2 (method B)

Method A. The reaction of 1-octene (**1a**)—chosen as a model for α -olefins—was carried out under conventional liquid-phase conditions, by adjusting an existing procedure.¹⁷ In a 25 mL round-bottomed flask, the catalyst (0.56 g, 7%) was activated at 550 °C; then, at 35 °C, a 5×10^{-1} M solution (10 mL) of 1-octene (5 mmol) in *n*-heptane or toluene, was introduced and kept magnetically stirred for 2 hours. After this time, ~70% conversion of 1-octene was reached, that corresponded to the equilibrium composition of metathesis products: between 70 and 80% as reported elsewhere for 1-octene.¹⁸ The molar ratio **1a**:Re was 23.7. All operations (catalyst activation, transfer of the solution, and reaction step) were carried out under a N_2 atmosphere.¹⁹ The course of the reaction was monitored by GC-MS.

Method B. The metathesis of 1-octene was then performed in dense CO_2 . In order to compare the results of methods A and B, identical amounts of the olefin **1a** and the catalyst (5 mmol of 1-octene; molar ratio **1a**:Re = 23.7) were used in both cases. The reaction was run for 2 h, sufficient to reach the equilibrium composition of metathesis products in this case also, as indicated by the fact that conversion did not increase further for longer

reaction times. Preliminary experiments showed that at 35 °C in a 30 mL autoclave, a homogeneous solution of **1a** (5 mmol) in CO_2 was obtained at pressure ≥ 80 bar.²⁰ A first set of tests was then executed at 90 bar where the CO_2 density (0.66 g/mL) was very similar to that of *n*-heptane (0.67 g/mL).²¹ Since previous methodologies were not available, the entire apparatus needed to be arranged. A Schlenk system was assembled to perform multiple operations under an inert (N_2) atmosphere. In particular: i) the high-temperature activation of the catalyst in a glass flask;²² ii) the charging of the catalyst and of the reactant olefin in a stainless-steel reactor (a 30 mL autoclave); iii) the reaction step in the autoclave, at CO_2 pressures ≥ 90 bar. Fig. 1 shows a schematic diagram of the system.

In all cases, regardless of the solvent used, the formation of the expected product of self-metathesis (7-tetradecene, **2a**) was accompanied by different co-products which were identified as isomers of 1-octene (2-, 3-, and 4-octene) and linear olefins $\text{C}_9\text{--C}_{13}$ (Scheme 1).



Scheme 1 Self- and cross-metathesis reactions were catalysed by supported Re_2O_7 . The isomerization (i) of 1-octene was promoted by the support ($\gamma\text{-Al}_2\text{O}_3$ or SiO_2) alone.

This behaviour was in line with that already reported for the metathesis of α -olefins carried out in the liquid phase.^{17,18,23} In particular, the isomerisation reaction could occur either due to the acidic sites of the support,^{22b} or by an addition–elimination sequence mediated by a metal-hydride species as observed elsewhere for Ru.²⁴ Higher internal olefins ($\text{C}_9\text{--C}_{13}$) derived from the cross-metathesis of the reagent **1a** and of its isomers.²⁵

Table 1 Re_2O_7 supported catalysts

	Precursor	Re (wt%) ^a	Support		Source	Cat. label	Particle size (nm) ^c
			Type	S_A [m ² /g] ^b			
1	NH_4ReO_4	6.8	$\gamma\text{-Al}_2\text{O}_3$	257	Puralox-Condea	Re-A ₁	<1
2	NH_4ReO_4	7.0	$\gamma\text{-Al}_2\text{O}_3$	200	Alfa-Aesar	Re-A ₂	<1
3	NH_4ReO_4	6.4	$\gamma\text{-Al}_2\text{O}_3$	257	Puralox-Condea	Re-A ₃	<1
4	NH_4ReO_4	6.7	SiO_2	550	Aldrich	Re-S	

^a The metal content was determined by optical ICP. ^b Surface area of the support. (Typically, the S_A for metathesis catalysts is ≥ 200 m²/g; ref. 1). ^c Determined by TEM.

Table 2 Self-metathesis of 1-octene in different solvents using supported Re₂O₇ catalysts^a

Entry	Cat.	Solvent ^b	X_{1a}^c ($\times 10^{-2}$) (mol:mol)	Conv.'n (%) (GC) ^d	Products (%) (GC)			Selectivity (%) ^h	Y (%) ⁱ
					Iso ^e	C ₉ -C ₁₃ ^f	2a ^g		
1	Re-A ₁	<i>n</i> -Heptane	7.3	67	1	4	62	92	62
2	Re-A ₂			46	1	1	44	96	
3	Re-S			1	1	—	—	—	
4	Re-A ₁	Toluene	1.1	40	1	1	38	95	
5	Re-A ₁		5.4	65	1	2	62	95	
6	Re-S			<1	<1	—	—	—	
7	Re-A ₁		1.1	36	1	1	34	95	
8	Re-A ₁	scCO ₂	1.1	71	1	2	68	97	67
9	Re-A ₂			37	1	2	32	86	
10	Re-S			<1	<1	—	—	—	

^a All reactions were carried out at 35 °C for 2 hours, using 1-octene (5 mmol) and the catalyst (0.56 g) in the molar ratio olefin:Re = 23.7. ^b *n*-Heptane and toluene: 10 mL of a 5×10^{-1} M solution of **1a**; scCO₂: 90 bar ($V = 30$ mL, $d = 0.66$ g/mL). ^c X_{1a} = mole fraction of 1-octene in the 1-octene/solvent solution. ^d The reaction conversion (% by GC) was referred to all metathesis (olefins C₉-C₁₄) and isomerization compounds (Scheme 2). ^e Total amount (% by GC) of isomerization by-products (2-, 3- and 4-octene). ^f Total amount (% by GC) of products of the cross-metathesis reaction (olefins C₉-C₁₃). ^g Total amount (% by GC) of 7-tetradecene: geometric isomers *trans/cis* were in ratio 3.8-4.0. ^h Selectivity towards the product of self-metathesis: [C₁₄ (Area%, GC)/conversion (%)] $\times 100$. ⁱ Isolated yields of crude **2a**.

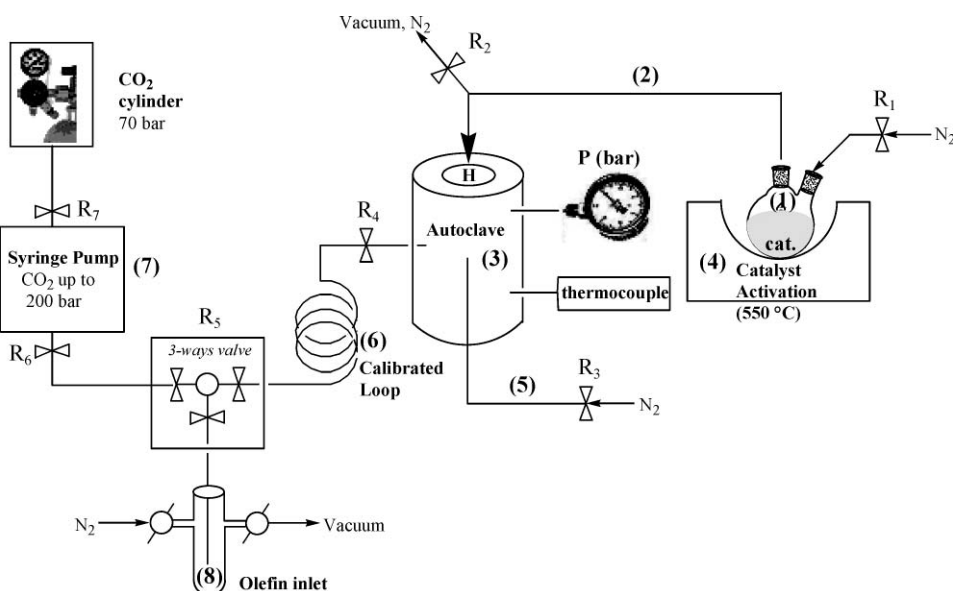
**Fig. 1** Schematic diagram of the apparatus used to carry out the metathesis of olefins in dense CO₂.

Table 2 reports the results of the self-metathesis of 1-octene using different solvents and different catalysts. Iso, C₉-C₁₃, and C₁₄ refer to the amounts (by GC) of isomerization products (total of 2-, 3-, and 4-octene), of cross-metathesis compounds (total of C₉-C₁₃), and of 7-tetradecene (total of *cis/trans* isomers), respectively. The reaction selectivity refers only to the formation of the self-metathesis product (**2a**).

The first significant aspect, never previously reported, was that scCO₂ could act as a solvent for the metathesis of 1-octene catalyzed by supported Re-oxide (entries 7-9). Other features emerging from Table 2, were: i) regardless of the solvent, only catalysts prepared from γ -Al₂O₃ were active for the transformation (entries 1, 2, 4, 5, 7 and 8); ii) the influence of the support was rather similar in the three tested solvents. In particular, the best system was Re-A₁ (on alumina Puralox, $S_A = 257$ m²/g), which allowed, after 2 h, conversions of 67, 65, and 71%, in *n*-heptane, toluene, and scCO₂, respectively

(entries 1, 5 and 8). The reaction conversions were lower on Re-A₂ (on alumina Alfa-Aesar, $S_A = 200$ m²/g): 46 and 37% in *n*-heptane and scCO₂ (entries 2 and 9). The silica-supported catalyst was not active at all (entries 3, 6 and 10); iii) finally, the selectivity towards the product of self-metathesis (7-tetradecene) was always very high (up to 96%). This compound (**2a**) was isolated from mixtures of reactions carried out in the presence of both *n*-heptane and scCO₂ solvents (conditions of entries 1 and 7): yields of crude 7-tetradecene (98% pure by GC) were 62% (305 mg) and 67% (340 mg), respectively.

Finally, two recycling experiments were performed using the Re-A₂ catalyst. After the reaction was carried out in the presence of scCO₂ (Table 2), Re-A₂ was filtered, dried under vacuum, and re-activated according to the procedure described above (N₂, 550 °C, 1.5 h). The catalyst was then re-used under the conditions of entry 9 (CO₂, 90 bar, Table 2). This cycle (activation/reaction) was repeated once more. The two reactions gave results in line

with the previous one (entry 9): the conversions were 39 and 33%, respectively, and the selectivity for 7-tetradecene was 99% in both cases. The catalyst recycle was not further investigated.²⁶

An issue of the reactions shown in Table 2 relates to the concentration of 1-octene in the different solvents: it is readily apparent that the reactant was significantly more concentrated in *n*-heptane and toluene (0.54 M) than in CO₂ (0.17 M). While the molar concentration is a convenient parameter to compare kinetic profiles in liquid solvents, it is not suitable for supercritical solvents as it does not take into account pressure and the related significant solvation effects. The mole fraction of 1-octene **1a** $\{X_{1a} = [\mathbf{1a}]/([\mathbf{1a}] + [\text{solvent}])\}$ appeared like a more appropriate parameter for a coherent comparison. In fact, in the experiments of Table 2, X_{1a} was also much larger in *n*-heptane and toluene (7.3×10^{-2} and 5.4×10^{-2} respectively) than in dense CO₂ (1.1×10^{-2}). Therefore, the metathesis was carried out in *n*-heptane and toluene with the same mole fraction of 1-octene $X_{1a} = 1.1 \times 10^{-2}$ as in scCO₂ (entries 4 and 7), using Re-A₁ as the catalyst. All else being equal, the conversion in these instances after 2 h were significantly lower (40% and 36% respectively, entries 4 and 7) with respect to the reaction in dense CO₂ (71%, entry 8). This indicated that the metathesis reaction was faster in the supercritical medium than in liquid solvents.

To further investigate the dilution effect, two more reactions were carried out in scCO₂ (90 bar, 35 °C), using more diluted solutions of the substrate. With respect to the above described conditions (method B), in the new experiments, the amount of olefin was decreased to 3.7 and 2.5 mmol, which corresponded to mole fractions (X_{1a}) of 0.5×10^{-2} and 0.8×10^{-2} , respectively. The quantity of the catalyst (Re-A₁) was also reduced to 0.42 and 0.28 g, in order to keep the molar ratio olefin:Re constant at 23.7 (method B). The results are illustrated in Fig. 2, where the conversion and the selectivity of the reaction, are plotted against the mole fraction of the olefin. To complete the view, the figure also includes the case of entry 8 of Table 2.

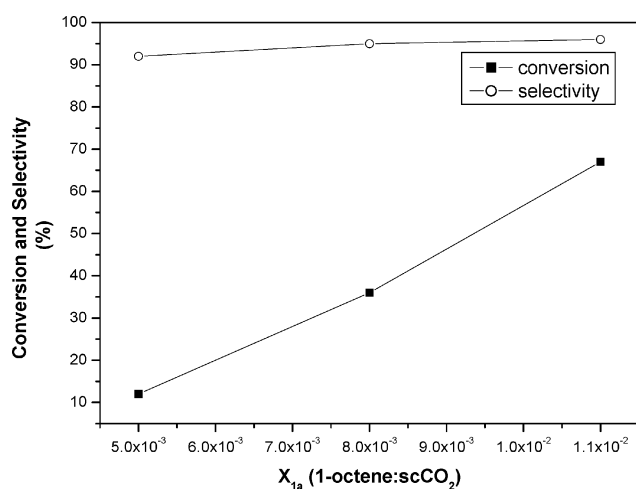


Fig. 2 Conversion of 1-octene and self-metathesis selectivity after 2 hours of reaction in scCO₂.

The overall effect of dilution was to decrease the rate of the process: when the mole fraction X_{1a} was halved (from 1.1×10^{-2} to 0.5×10^{-2}), the conversion of 1-octene dropped considerably from 71 to 12% (■ line in Fig. 2). By contrast,

the self-metathesis selectivity (92–97%, ○ line in Fig. 2) was not appreciably modified by the change of X_{1a} . This behaviour was similar to that observed in the presence of *n*-heptane and toluene as solvents (compare entries 1 and 4, and 5 and 7 of Table 2).

The effect of the CO₂ pressure

The solvating ability of supercritical carbon dioxide can be controlled by adjusting density and viscosity through small variations of pressure and temperature.²⁷ This behaviour allows one to fine-tune the solvent power of scCO₂, and can be exploited to improve the performance of several processes.^{8,25}

A set of experiments were devised to investigate the effect of the CO₂ pressure under the conditions set up for the metathesis on solid catalysts. The above-described method B (35 °C; 5 mmol of **1a**; molar ratio **1a**:Re = 23.7, 2 h), was used to carry out the reaction of 1-octene at 80, 120 and 150 bar, in the presence of Re-A₁ as the catalyst. The results are shown in Fig. 3, where the conversion and the selectivity of the process are plotted against the CO₂ pressure. To complete the view, the figure also includes the data obtained at 90 bar (entry 8, Table 2). At the different pressures, the values of the density of CO₂ are indicated in parenthesis.

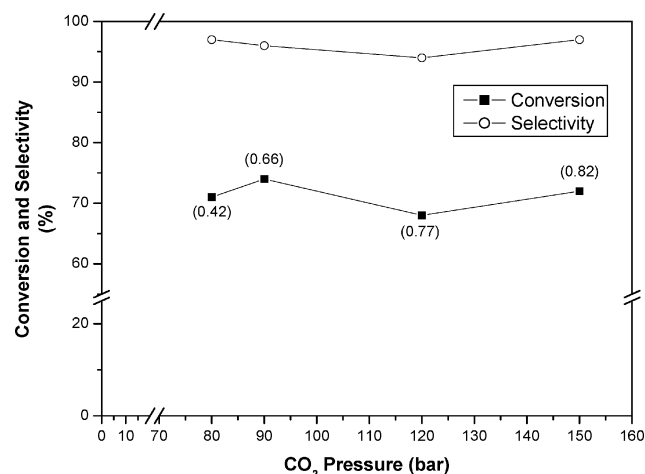


Fig. 3 The self-metathesis of 1-octene: conversion and selectivity as a function of the CO₂ pressure. The values of the CO₂ density (taken from ref. 21) are shown in parenthesis.

The change of the CO₂ pressure in the range from 80 to 150 bar did not affect the reaction outcome: both the conversion of 1-octene and the self-metathesis selectivity remained substantially constant at nearly 70% and 95%, respectively. It should be promptly noted that this behaviour implied an apparent incongruity. In fact, since the increase of the pressure (and of the density) of the supercritical medium entailed a decrease of the mole fraction of the olefin (80 bar: $X_{1a} = 1.7 \times 10^{-2}$; 150 bar: $X_{1a} = 0.9 \times 10^{-2}$), a significant drop of the reaction conversion would have been expected (compare Tables 2 and Fig. 1). A comment is offered in the Discussion section.

The effect of the catalyst amount

In the presence of scCO₂, the influence of the catalyst amount on the metathesis of 1-octene, was studied using the Re-A₃

Table 3 The effect of the catalyst amount on the self-metathesis of 1-octene carried out in scCO₂ (35 °C, 90 bar)^a

Entry	Catalyst	1a:Re ^b (mol:mol)	<i>t</i> (h)	Conv. 'n (%) ^c	Sel. (%) ^c	TOF × 10 ⁻² (mol/mol min) ^d
1	Re-A ₃	47.4	2	39	85	15
2	Re-A ₃	23.7	2	71	96	14
3	Re-A ₃	15.8	2	82	94	11
4	Re-A ₃	11.8	2	81	93	8
5	Re-A ₃	11.8	1	64	94	13

^a All reactions were carried out following the general procedure described as method B. ^b 1a:Re was the molar ratio 1-octene:Re. ^c The reaction conversion and the self-metathesis selectivity were defined as reported in Table 2. ^d TOF: mole of converted olefin per mole of Re per minute.

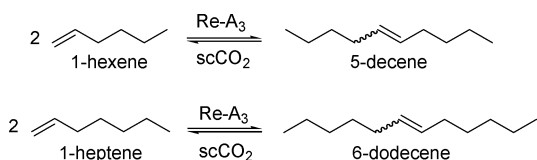
sample (Table 1). According to the method B (see above), five subsequent experiments were performed by setting the molar ratio 1a:Re at 47.4, 23.7, 15.8, and 11.8, respectively. Other parameters such as temperature and pressure (35 °C and 90 bar) and the olefin amount (5 mmol) were not altered. Results are reported in Table 3.

After 2 hours of reaction, doubling the amount of catalyst increased the conversion from 39 to 71% (1a:Re ratio was halved from 47.4 to 23.7; entries 1–2). Further increments of the catalyst amount (1a:Re at 15.8 and 11.8, respectively) produced only a moderate change: the substrate conversion reached a substantially constant value slightly over 80% (entries 3–4), that did not increase further for longer reaction times.

This behaviour along with the calculated turnover frequency (TOF: moles of converted olefin per mole of Re per minute), suggested that a ratio 1a:Re in the range of 23.7–15.6 allowed the metathesis of 1-octene to achieve equilibrium in the first 120 min. If a higher amount of catalyst was used (1a:Re of 11.8), a lower specific activity resulted (entry 4, TOF = 8 min⁻¹): under these conditions, the equilibrium was perhaps reached more quickly. The last experiment corroborated this hypothesis. Operating at the highest catalyst loading (1a:Re of 11.8), the conversion was 64% after only 1 hour, and the corresponding TOF went up to 13 min⁻¹ (entry 5), in line with the values obtained in the previous reactions (TOF = 14–15, entries 1–2). The self-metathesis selectivity was at the same high level (93–96%) reported in Tables 2 and 3 and Fig. 2 and 3, except for the lower catalyst amount (1a:Re of 47.4): in this case, the selectivity dropped to 85% (entry 1), due to the onset of the isomerization reaction whose products summed to 7% (by GC).

The self-metathesis of 1-hexene and 1-heptene in scCO₂

In the presence of the Re-A₃ catalyst, the metathesis of other α-olefins such as 1-hexene and 1-heptene (1b and 1c, respectively), was investigated in supercritical carbon dioxide as the solvent (Scheme 2).

**Scheme 2**

The reaction conditions were those of entry 8 in Table 2. Both reactions proceeded very similarly to that of 1-octene (Table 4). At 35 °C (90 bar), after 2 hours, conversions were

Table 4 The self-metathesis of 1-hexene and 1-heptene carried out in scCO₂ (35 °C, 90 bar)^a

Entry	Catalyst	Substrate	Conv. 'n (%) ^b	Products (% GC) ^c			Sel. (%) ^d
				Iso	Cross	Self	
1	Re-A ₃	1-Hexene	64	1	2	61	95
2	Re-A ₃	1-Heptene	67	2	2	63	94

^a All reactions were carried out for 2 hours, at 35 °C, in the presence of Re-A₃ as the catalyst. Experiments were run under the conditions of entry 8 in Table 2, by using a mixture of α-olefin (5 mmol) and the catalyst (0.56 g) in the molar ratio olefin:Re = 23.7. ^b The reaction conversion was determined by GC. ^c Products. Iso: total amount of isomers of 1-hexene (2- and 3-hexene, entry 1) and of 1-heptene (2- and 3-heptene, entry 2); Cross: total amount of products of cross-metathesis of 1-hexene (olefins C₇–C₉, entry 1) and of 1-heptene (olefins C₈–C₁₁, entry 2); Self: amount of the product of self-metathesis of 1-hexene (5-decene, entry 1) and of 1-heptene (6-dodecene, entry 2). ^d The selectivity was defined towards the product of self-metathesis. Entry 1: [C₁₀ (Area%, GC)/conversion (%)] × 100; entry 2: [C₁₂ (Area%, GC)/conversion (%)] × 100.

64 and 67% for 1-hexene and 1-heptene, respectively. The self-metathesis selectivity was 94 and 95%, and the structures of the corresponding products (5-decene and 6-dodecene) were assigned by GC-MS and by comparison to authentic samples.

Reproducibility

A total of nearly 120 experiments were carried out (including reactions, not here reported, to evaluate conversions vs. time, and to reproduce results of Tables 2 and 3 and Fig. 2 and 3) during the examination of the metathesis of 1-octene in both scCO₂ and conventional liquid solvents. Both the conversion and the self-metathesis selectivity (determined by GC-MS) were reproducible within a range of ±5%. It should be mentioned however, that 15 out of the total number of the tests showed a conversion less than 10%, and most of these unsuccessful trials (12) were observed in *n*-heptane.²⁸ Presently, no clear reasons account for this behaviour.

Discussion

CO₂ as a solvent for metathesis

Although the use of scCO₂ as a metathesis solvent in place of traditional organic solvents, represents an improvement towards greening the process, by itself it is not necessarily an innovation. It becomes such only when scCO₂ contributes to enhance other aspects of the chemical transformation as well, particularly if it

makes the reaction faster compared to traditional conditions, or if it overcomes a technological barrier towards more efficient operation.

One such instance where scCO_2 has a significant advantage over traditional solvents is when it is used to overcome the mass transfer limitations associated with heterogeneous catalysis. This is exemplified by the present case where Re-based solid catalysts, prepared by impregnation of Re on commercial alumina supports, were shown to be active for the metathesis of olefins when combined with the use of compressed CO_2 as a solvent (Table 2). ScCO_2 promoted the self-metathesis of 1-octene over these supported Re catalysts with higher conversion compared to conventional liquid solvents. The properties of the supercritical medium account for this behaviour. For one, the gas-like diffusivity and viscosity and the liquid-like density of scCO_2 , as well as the elimination of interphases, result in a significant improvement of the mass transfer. In addition, peculiar solvation phenomena are known to take place. These can be described as local density enhancements (LDEs), whereby the density as well as the composition of the local environment around the solute molecules are modified, with respect to the bulk of the supercritical solvent.^{8,11}

The outcome of the self-metathesis is sensitive to the concentration of the olefin solution: the more diluted the substrate, the lower the conversion (Fig. 2). However, when the pressure (*i.e.* the density) of CO_2 is increased in the range of 80–150 bar, thereby diluting the reactant olefin, the expected drop of conversion is not observed (Fig. 3). Different aspects can account for this apparent inconsistency. On one side, the enhancement of the pressure may have a beneficial influence: in dense CO_2 , it is often reported that kinetic profiles, yields, and selectivity of a variety of reactions, are improved by increasing the density of the medium.^{8,11,25} On the other hand, by operating at high pressure in a closed system, the equilibrium is different from an open system due to the release of stoichiometric amounts of ethylene that could prove disadvantageous for a reaction such as metathesis. However, being the total pressure almost exclusively determined by the CO_2 , the release of ethylene and the equilibrium should not be affected.^{7b,29} In the case investigated here, these opposite effects seem counterbalanced in such a way that the final pressure (and density) of the supercritical solvent does not affect the macroscopic outcome of the process.

The influence of the catalyst

The most significant aspect deals with the nature of the supports ($\gamma\text{-Al}_2\text{O}_3$ and silica). It is generally agreed that the monomeric tetrahedral structure of ReO_4^- , is stabilized over the alumina surface: the metal centre forms three equivalent $\text{Re}=\text{O}$ moieties and a $\text{Re}-\text{O}-\text{Al}$ bond with an acidic OH group on the support.^{18,30} Although the nature of this last interaction is not fully understood, a high surface area (S_A) of the solid alumina is crucial to increase the dispersion of the active phase and to improve the catalytic performance.³¹ This reason may account for the behaviour reported in Table 2: in the presence of both scCO_2 and *n*-heptane as a solvent, the Re- A_1 sample supported on a $\gamma\text{-Al}_2\text{O}_3$ of 257 m^2/g , allows a higher conversion with respect to the Re- A_2 catalyst prepared on a $\gamma\text{-Al}_2\text{O}_3$ of 200 m^2/g . However, definite conclusions on metal dispersion

and particle size cannot be drawn yet. The TEM analysis of Re- A_1 and Re- A_2 shows the γ -phase in the shape of grains of 5–6 nm, while the Re-oxide particles are not clearly distinguishable, their size being less than 1 nm. Onaka *et al.* have reported a similar result.¹⁸

Silica possesses a lower surface acidity with respect to alumina.³² This difference is claimed to explain the generally poorer activity of silica-supported Re-oxide in the metathesis of olefins.³³ An example is the metathesis of 1-butene which is reported to take place at temperatures not below 75 °C, in the presence of a $\text{Re}_2\text{O}_7/\text{SiO}_2$ (6%) catalyst.³⁴ The results of Table 2 can be discussed on a similar basis: plausibly, the Re-S sample (on silica) is not effective for the reaction of 1-octene, because of the low reaction temperature (35 °C).

As far as the amount of the catalyst, Table 3 suggests that in the presence of a relatively low metal loading (7%),³⁵ a convenient olefin:Re molar ratio is in the range of 20–25. Under these conditions, in supercritical CO_2 (90 bar, 35 °C, $d = 0.66 \text{ g/mL}$), the substrate conversion reaches an equilibrium value of ~ 70% after the first 120 min of reaction.

Conclusions

This paper describes the first example of self-metathesis of α -olefins (1-hexene, 1-heptene, and 1-octene) catalysed by heterogeneous Re-based catalysts, in the presence of supercritical carbon dioxide as the solvent. Although an additional “compression” energy (and costs) must be provided with respect to traditional solvent systems, in the present case, beyond the environmentally benign character of scCO_2 , a remarkable improvement of the reaction outcome is observed: for example, at 35 °C, the self-metathesis of 1-octene proceeds with a conversion over 30% higher on average in the supercritical medium than in a conventional solvent such as *n*-heptane. A performance possibly due to the increase of the mass transfer promoted by dense CO_2 . The reaction of 1-octene is also plausibly affected by the enhancement of the pressure of CO_2 , through opposite actions: on one hand, a beneficial solvation/mass transfer effect may operate; on the other, disadvantages may derive from the dilution of the substrate. The final result is that in the range of 80–150 bar, both the conversion and the self-metathesis selectivity show no appreciable variations.

The most significant influence of the catalysts, deals with the nature of their support. In the presence of $\gamma\text{-Al}_2\text{O}_3$, the catalytic systems are active, and their performance seems improved by the increase in the surface area of the solid matrix. By contrast, if Re-oxide is dispersed over the less acidic silica (with respect to alumina), no reaction takes place at all. This behaviour is observed in both scCO_2 and *n*-heptane solvents.

Overall, scCO_2 appears as a viable alternative for the replacement of liquid solvents ordinarily used in the metathesis of olefins. Not only the sustainability of the process is improved, but the novelty of this finding opens a new perspective in a field which is still largely unexplored.

Experimental

General. α -Olefins **1a-c** were ACS grade and were employed without further purification. Conventional liquid solvents

(*n*-heptane and toluene), were either used as such or purified through known methods.³⁶ Ammonium perrhenate (NH₄ReO₄, ≥99%) was from Aldrich. γ-Al₂O₃ was from two different sources: Puralox-Condea and Alfa-Aesar. These solids had a surface area (*S*_A) of 257 and 200 m²/g, respectively. Silica was from Aldrich (*S*_A = 550 m²/g). GC-MS (70 eV) analyses were run using a HP5/MS capillary column (30 m). The gaseous N₂ used throughout the activation of catalysts and the general procedure for the reaction (see below), was of an R-grade and it was further purified by Drierite®/13X filters (Aldrich). Wherever used, water was of milli-Q grade. CO₂ was of a SFC/SFE grade (purity 99.998%). ¹H NMR spectra were recorded on a 300 MHz spectrometer, using CDCl₃ as solvent.

The preparation of catalysts

All catalysts were prepared by a wet-impregnation technique described in the literature.^{5c,37} A 25 mL round bottomed flask was charged with an aqueous solution (1.7 × 10⁻¹ M, 12 mL) of NH₄ReO₄ (555 mg, 2.1 mmol) and with the chosen support (γ-Al₂O₃ or silica; 5 g). The slurry was kept under magnetic stirring for 1 hour at rt, and then dried under vacuum (50 °C, 36 mbar). The solid residue was further wetted with water (8 mL), stirred for 15 min at rt, and finally, dried again (50 °C, 2 mbar). The solid sample was placed in a tubular quartz reactor and calcined in a stream of dried air (~80 mL/min). The final calcination temperature (550 °C) was reached through a ramp of 10 °C/min, and it was kept for 4 hours. Three catalysts were supported on two different aluminas, while a fourth specimen was dispersed on SiO₂. They were labelled as Re-A₁, Re-A₂, Re-A₃, and Re-S, respectively.

The characterization of catalysts

Systems Re-A₁, Re-A₂ and Re-A₃ were characterized by optical ICP and TEM. In order to perform ICP analyses, solid samples were digested through the following procedure: a Teflon-lined autoclave (200 mL) was charged with the catalyst (0.05 g), water (5 mL), aq HF (40%, 1.5 mL), and a mixture of aq HCl/HNO₃ (3:1 v/v; 3 mL). The autoclave was then closed with a Teflon-lined cap, and heated in a microwave digestion rotor (MDS 2000) at 170 °C, for 1 hour. After being cooled to rt, the clear solution was transferred into a volumetric flask and diluted with water to 50 mL. Then, ICP analyses were carried out at 197.248 nm (power of 1400 W). In the three catalytic samples, the Re content was of 6.8, 7.0 and 6.4, respectively (Table 1).

TEM analysis was carried out with a JEM 3010 (JEOL) electron microscope operating at 300 kV, point to point resolution at Scherer defocus of 0.17 nm. A suspension of the catalytic sample (20 mg) in *i*-propanol was sonicated for 5 min. Then, an aliquot (5 μL) was poured on a copper grid coated with amorphous carbon. At rt, once *i*-propanol was evaporated, the sample was ready for the analysis.

TEM measures showed the presence of grains of γ-Al₂O₃ with an average size of 5–6 nm. Instead, the particles of Re-oxide were not clearly visible, their dimensions being lower than 1 nm. Fig. 4 shows the TEM images of the ReA₁ catalyst.

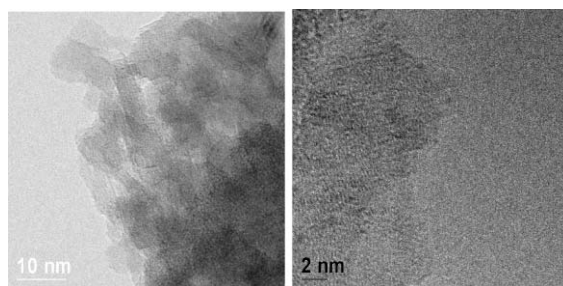


Fig. 4 TEM images of the ReA₁ catalyst.

General procedures for the metathesis of 1-octene

Two procedures (methods A and B) were used. In both cases, since heterogeneous catalysts for the metathesis of alkenes were extremely sensitive to air and humidity, all operations required a strictly inert atmosphere.

Method A. This method was devised for reactions performed with conventional liquid solvents (*n*-heptane and toluene). The catalyst, Re₂O₇ supported on γ-Al₂O₃ or on SiO₂ (0.56 g, 7%), was charged in a 25 mL 3-necked round bottomed flask, equipped with two stopcocks and a screw-thread adapter capped with a rubber septum. A magnetic stirring bar was hung on the top of the adapter, by a small external magnet.³⁸ At rt, three N₂/vacuum cycles were performed, and the system was kept under a N₂ stream of 50 mL/min. The flask was placed in an electric oven and heated up to 550 °C. This temperature was reached through a ramp of 10 °C/min, and it was maintained for 1.5 hours. The heating operation was checked by a thermocouple positioned on the bottom of the flask.

During the activation step, the colour of the catalyst showed some peculiar changes: the white powder (initially charged in the flask) turned to a gray tonality around 400 °C, then a black colour was persistent at 550 °C. After 1 h at this temperature, the powder began to fade until a pale yellow solid was obtained at the end of the heating time. This was the final colour of the catalyst used in the reaction.

After cooling at rt, the flask was thermostated at 35 °C, and the stirring bar was released over the solid catalyst. A solution of 1-octene in *n*-heptane (Table 2: 5 × 10⁻¹ M, 10 mL; Table 3: 0.7 × 10⁻¹ M, 70 mL) was degassed, transferred over the activated catalyst, and kept under a static N₂ atmosphere.³⁹ The suspension was magnetically stirred (450 rpm) for 2 hours, cooled to rt, and finally vented. An aliquot (0.5 mL) of the final mixture was centrifuged and analysed by GC-MS.

Method B. Method B was specifically conceived for the use of dense CO₂ as the solvent. Fig. 1 illustrates the apparatus specifically designed to the scope.

SAFETY WARNING

Operators of high pressure equipment should take proper precautions to minimize the risks of personal injury.⁴⁰

The catalytic activation was carried out under conditions identical to those above-described for method A, with one difference: the flask (1) was connected to a glass adapter (2) sealed at the autoclave top aperture (H), by a rubber conic ring. In this way, the N₂ stream coming out from the flask, was

conveyed directly in the autoclave (3) throughout the activation step. Once this operation was concluded, at rt, the flask was rotated along the axis of the adapter (2), to let the catalyst slide in the autoclave. Thanks to a supplementary gas line (5), the N₂ flow was enhanced up to 150 mL/min, the adapter (2) was rapidly removed, and the reactor was finally closed. The reactant olefin (1-octene, 0.56 g, 5 mmoles), preliminary charged in a 4 mL vial (8), was degassed under vacuum and loaded in a 1 mL calibrated loop (6). From here, the olefin was transferred in the autoclave under a CO₂ stream generated through a syringe pump (ISCO 260D, 7). Unless otherwise specified, the molar ratio 1-octene:Re was 23.7. The reactor was pressurized at approximately 60 bar and electrically heated at the desired temperature (35 °C). The final pressure (80–150 bar) was reached by slowly adding the remaining CO₂. The mixture was magnetically stirred at ~500 rpm and its visual inspection was possible thanks to two sapphire windows assembled on both head and bottom of the autoclave. The reaction was allowed to proceed for 2 h. Then, after cooling at rt, CO₂ was slowly vented by bubbling it into a 5 mL vial of acetone. The content of the reactor was washed with additional acetone (5 mL), and the combined organic solutions were analyzed by GC-MS.

Fig. 5 exemplifies a typical GC-MS obtained for the self-metathesis of 1-octene catalyzed by Re₂O₇/γ-Al₂O₃ (7%, ReA₁ in Table 2 of the Result section), in the presence of dense CO₂ (90 bar, 35 °C, *d* = 0.66 g/mL) as solvent. Reaction conditions are those of entry 8 in Table 2.

Isolation and characterisation of 7-tetradecene. Since heterogeneous catalysts for the metathesis of alkenes are rather delicate systems, the mass balance of the reaction was never evaluated by addition of internal standards. However, using both method A and B, the product of self-metathesis of 1-octene (7-tetradecene) was obtained in yields of 62–68%, which well-matched conversions measured by GC-MS. Product **2a** was simply isolated by filtration of the catalyst and removal of the unreacted 1-octene under vacuum (50 °C/200 mbar). The

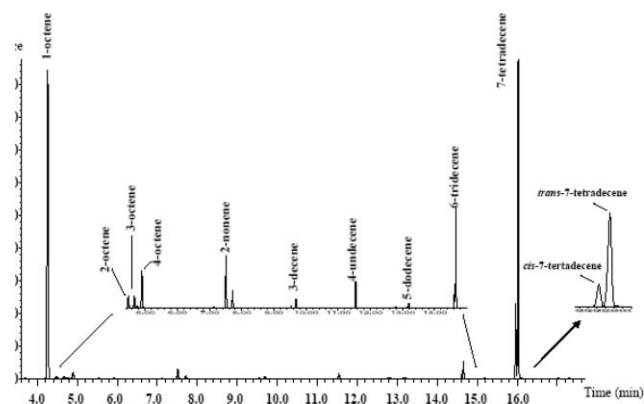


Fig. 5 GC-MS of the self-metathesis of 1-octene in dense CO₂. Enlargements are reported to detail *cis/trans* isomers of 7-tetradecene and products coming from isomerization and cross-metathesis reactions.

crude product was obtained as a pale-yellow liquid and it was characterized as such.

7-Tetradecene. ¹H NMR (300 MHz, CDCl₃) δ: 5.40 (2H, m), 1.99 (4H, m), 1.29 (16H, m), 0.90 (6H, t, *J* = 6.7 Hz). In the *cis/trans* mixture, vinylic hydrogens were centered at δ = 5.35 for the *cis* isomer, and at δ = 5.38 for the *trans* compound.¹⁸ The structure was also assigned by comparison with an authentic commercial sample (Aldrich # 227560).

trans-7-Tetradecene. GC-MS (relative intensity, 70 eV) *m/z*: 196 ([M]⁺, 24%), 111 (21), 98 ([M - (CH₂)₇]⁺, 18), 97 (50), 85 (12), 84 ([M - (CH₂)₈]⁺, 35), 83 (72), 82 (14), 71 (23), 70 ([M - (CH₂)₉]⁺, 63), 69 (100), 68 (12), 67 (21), 57 (43), 56 ([M - (CH₂)₁₀]⁺, 58), 55 (90), 54 (24). Database Wiley: Ref. 33342, match quality 97%.⁴¹

cis-7-Tetradecene. GC-MS (relative intensity, 70 eV) *m/z*: 196 ([M]⁺, 20%), 111 (21), 98 ([M - (CH₂)₇]⁺, 16), 97 (50), 85 (12), 84 ([M - (CH₂)₈]⁺, 34), 83 (68), 82 (16), 81 (11), 71 (24), 70 ([M - (CH₂)₉]⁺, 67), 69 (99), 68 (13), 67 (25), 57 (47), 56 ([M - (CH₂)₁₀]⁺, 66), 55 (100), 54 (23). Database Wiley: Ref. 33341, match quality 96%.⁴¹

Table 5 MS characterization of the reaction products of 1-octene

Compound	GC-MS (relative intensity, 70 eV)	Match quality (%) (Ref. Wiley)
1-Octene	<i>m/z</i> : 112 ([M] ⁺ , 11%), 84 ([M - (CH ₂) ₂] ⁺ , 23), 83 (39), 71 (12), 70 ([M - (CH ₂) ₃] ⁺ , 88), 69 (50), 57 (16), 56 ([M - (CH ₂) ₄] ⁺ , 86), 55 (100), 54 (11), 53 (10)	91 (116372)
2-Octene	<i>m/z</i> : 112 ([M] ⁺ , 40%), 84 ([M - (CH ₂) ₂] ⁺ , 10), 83 (21), 70 ([M - (CH ₂) ₃] ⁺ , 53), 69 (29), 57 (18), 56 ([M - (CH ₂) ₄] ⁺ , 53), 55 (100), 54 (10)	91 (3597)
3-Octene	<i>m/z</i> : 112 ([M] ⁺ , 39%), 83 (19), 70 ([M - (CH ₂) ₃] ⁺ , 55), 69 (32), 57 (19), 56 ([M - (CH ₂) ₄] ⁺ , 52), 55 (100), 53 (10)	64 (3598)
4-Octene	<i>m/z</i> : 112 ([M] ⁺ , 41%), 84 ([M - (CH ₂) ₂] ⁺ , 11), 83 (19), 70 ([M - (CH ₂) ₃] ⁺ , 53), 69 (35), 57 (20), 56 ([M - (CH ₂) ₄] ⁺ , 55), 55 (100), 54 (10)	80 (116369)
2-Nonene	<i>m/z</i> : 126 ([M] ⁺ , 33%), 97 (17), 84 ([M - (CH ₂) ₃] ⁺ , 15), 83 (13), 70 ([M - (CH ₂) ₄] ⁺ , 42), 69 (38), 57 (11), 56 ([M - (CH ₂) ₅] ⁺ , 61), 55 (100), 54 (11)	83 (6385)
3-Decene	<i>m/z</i> : 140 ([M] ⁺ , 5%), 111 (14), 98 ([M - (CH ₂) ₃] ⁺ , 13), 97 (32), 84 ([M - (CH ₂) ₄] ⁺ , 26), 83 (39), 82 (11), 71 (10), 70 ([M - (CH ₂) ₅] ⁺ , 90), 69 (70), 68 (11), 67 (12), 57 (62), 56 ([M - (CH ₂) ₆] ⁺ , 100), 55 (89), 54 (13), 53 (10)	—
4-Undecene	<i>m/z</i> : 154 ([M] ⁺ , 32%), 97 (20), 84 ([M - (CH ₂) ₅] ⁺ , 23), 83 (35), 71 (10), 70 ([M - (CH ₂) ₆] ⁺ , 53), 69 (76), 67 (16), 57 (22), 56 ([M - (CH ₂) ₇] ⁺ , 59), 55 (100), 54 (14)	94 (15562)
5-Dodecene	<i>m/z</i> : 168 ([M] ⁺ , 33%), 111 (11), 98 ([M - (CH ₂) ₅] ⁺ , 12), 97 (29), 84 ([M - (CH ₂) ₆] ⁺ , 26), 83 (45), 82 (10), 71 (12), 70 ([M - (CH ₂) ₇] ⁺ , 53), 69 (79), 67 (15), 57 (28), 56 ([M - (CH ₂) ₈] ⁺ , 56), 55 (100), 54 (17)	97 (21249)
6-Tridecene	<i>m/z</i> : 182 ([M] ⁺ , 44%), 111 (18), 98 ([M - (CH ₂) ₆] ⁺ , 15), 97 (43), 84 ([M - (CH ₂) ₇] ⁺ , 30), 83 (61), 82 (12), 71 (18), 70 ([M - (CH ₂) ₈] ⁺ , 59), 69 (100), 67 (17), 57 (34), 56 ([M - (CH ₂) ₉] ⁺ , 54), 55 (82), 54 (19)	—

Products of isomerization of 1-octene and of cross-metathesis.

These compounds (see Fig. 5) were identified by GC-MS analyses, and their structures were assigned by comparison to standard products included in the Wiley Library of Mass spectral data.⁴¹ Table 5 reports molecular ions, the main fragmentation pattern, and the match quality obtained for each compound.

Self-metathesis of 1-hexene and 1-heptene

Method B was used also to carry out the self-metathesis of 1-hexene and 1-heptene (Table 5). The olefin amounts were of 5 mmol in both cases (0.42 and 0.49 g for 1-hexene and 1-heptene, respectively) and the molar ratio olefin:Re was of 23.7. Both products were not isolated: their structures were assigned by GC-MS and by comparison to an authentic commercial sample (5-decene: Aldrich # 110485).

5-Decene. Compared to an authentic commercial sample from Aldrich Chemical Co. GC-MS (relative intensity, 70 eV) *m/z*: 140 ([M]⁺, 35%), 97 (17), 84 ([M - (CH₂)₄]⁺, 13), 83 (15), 70 ([M - (CH₂)₃]⁺, 38), 69 (46), 67 (10), 57 (11), 56 ([M - (CH₂)₆]⁺, 46), 55 (100), 54 (10). Database Wiley: Ref. 10399, match quality 90%.⁴¹

6-Dodecene. Recognized by comparison of its physical data with those in the literature.⁴² GC-MS (relative intensity, 70 eV) *m/z*: 168 ([M]⁺, 35%), 111 (11), 98 ([M - (CH₂)₅]⁺, 11), 97 (30), 84 ([M - (CH₂)₆]⁺, 26), 83 (43), 71, (13), 70 ([M - (CH₂)₇]⁺, 56), 69 (100), 67 (15), 57 (30), 56 ([M - (CH₂)₈]⁺, 53), 55 (82), 54 (18). Database Wiley: Rif. 21247, match quality 96%.⁴¹

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Notes and references

- (a) K. J. Ivin and J. C. Mol, In *Olefin Metathesis and Metathesis Polymerization*, Academic Press, 1997; (b) M. Schuster and S. Blechert, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 2036–2056; (c) A. M. Thayler, *Chem. Eng. News* 2007, 37–47.
- A. Mauren Rouhi, *Chem. Eng. News*, 2002, **80**, 34–38.
- W. F. Carroll, Jr. <http://pubs.acs.org/pressrelease/nobelprize/2005.html>.
- (a) R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, **54**, 4413–4450; (b) C. W. Bielawski and R. H. Grubbs, *Angew. Chem. Int. Ed. Engl.*, 2000, **39**, 2903–2906; (c) M. Chabanas, C. Coperet and J.-M. Basset, *Chem. Eur. J.*, 2003, **9**, 971–975.
- T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18–29.
- (a) S. Tamagaki, R. J. Card and D. C. Neckers, *J. Am. Chem. Soc.*, 1978, 6653–6639; (b) F. Kapteijn and J. C. Mol, *J. Chem. Soc. Faraday Trans. 1*, 1982, **78**, 2583–2592; (c) T. Kawai, Y. Yamazaki, T. Taoka and K. Kobayashi, *J. Catal.*, 1984, **89**, 452–461; (d) R. H. A. Bosma, F. van den Aardweg and J. C. Mol, *J. Organomet. Chem.*, 1985, **280**, 115–122; (e) R. Spronk and J. C. Mol, *Appl. Catal.*, 1991, **70**, 295–306; (f) L. R. Sita, *Macromolecules*, 1995, **28**, 656–657; (g) M. T. Crimmins and B. W. King, *J. Org. Chem.*, 1996, **61**, 4192–4193; (h) K. Melis, D. De Vos, P. Jacobs and F. Verpoort, *J. Mol. Catal.*, 2001, **169**, 47–56; (i) J. Aguado, J. M. Escola, M. C. Castro and B. Paredes, *Appl. Catal. A: General*, 2005, **284**, 47–57.
- (a) J. M. De Simone and C. D. Misteale, US Pat. 58400820 (Nov. 24, 1998); (b) A. Fürstner, L. Ackermann, K. Beck, H. Hori, D. Koch, K. Langemann, M. Liebel, C. Six and W. Leitner, *J. Am. Chem. Soc.*, 2001, **123**, 9000–9006; (c) A. Fürstner, W. Leitner, D. Koch, K. Langemann and C. Six, US Pat. 6348551 (Feb. 19, 2002); (d) W. Leitner, N. Theyssen, Z. Hou, K. W. Kottsieper, M. Solinas and D. Giunta, US Pat. 2006252951 (Nov. 09, 2006).
- A. Stark, M. Ajam, M. Green, H. G. Raubenheimer, A. Ranwell and B. Ondruschka, *Adv. Synth. Catal.*, 2006, **348**, 1934–1941.
- P. G. Jessop, T. Ikariya and R. Noyori, *Organometallics*, 1995, **14**, 1510–1513.
- (a) T. Groß, L. Chen and H.-D. Lüdemann, In *Supercritical Fluids as Solvents and Reaction Media*, Chapt. 2.1; G. Brunner, Ed.; Elsevier, 2004; (b) A. Baiker, *Chem. Rev.* 1999, **99**, 453–473.
- M. G. Hitzler, F. R. Smail, S. K. Ross and M. Poliakoff, *Chem. Commun.*, 1998, 359–360.
- (a) W. K. Gray, F. R. Smail, M. G. Hitzler, S. K. Ross and M. Poliakoff, *J. Am. Chem. Soc.*, 1999, **121**, 10711–10718; (b) C. Vieville, Z. Mouloungui and A. Gaset, *Ind. Eng. Chem. Res.*, 1993, **32**, 2065–2068.
- J. R. Hyde, P. Licence, D. Carter and M. Poliakoff, *App. Catal. A: General*, 2001, **222**, 119–131.
- (a) A. R. Tadd, A. Marteel, M. R. Manson, J. A. Davies and M. A. Abraham, *Ind. Eng. Chem. Res.*, 2002, **41**, 4514–4522; (b) A. E. Marteel, T. T. Tack, S. Bektsev, J. A. Davies, M. R. Manson and M. A. Abraham, *Environ. Sci. Technol.*, 2003, **37**, 5424–5431.
- L. Fan, T. Watanabe and K. Fujimoto, *Appl. Catal.*, 1997, **158**, L41–L46.
- (a) J. M. De Simone, M. Selva and P. Tundo, *J. Org. Chem.*, 2001, **66**, 4047–4049; (b) M. Selva and P. Tundo, *Acc. Chem. Res.*, 2002, **35**, 706–716; (c) M. Selva, P. Tundo and A. Perosa, *J. Org. Chem.*, 2002, **67**, 9238–9247; (d) M. Selva, P. Tundo and A. Perosa, *J. Org. Chem.*, 2003, **68**, 7374–7378; (e) A. Loris, A. Perosa, M. Selva and P. Tundo, *J. Org. Chem.*, 2003, **68**, 4046–4051; (f) M. Selva, P. Tundo, A. Perosa and F. Dall'Acqua, *J. Org. Chem.*, 2005, **70**, 2771–2777; (g) M. Selva, P. Tundo and T. Foccardi, *J. Org. Chem.*, 2005, **70**, 2476–2485; (h) F. Bonino, A. Damin, S. Bordiga, M. Selva, P. Tundo and A. Zecchina, *Angew. Chemie, Engl. Int. Ed.*, 2005, **44**, 4774–4777; (i) M. Selva and P. Tundo, *J. Org. Chem.*, 2006, **71**, 1464–1470; (j) P. Tundo, A. Loris and M. Selva, *Green Chem.*, 2007, **9**, 777–779.
- Among them, one of the most investigated and efficient system is Re₂O₇ on γ-Al₂O₃, with a metal content ranging from 5 to 18%. See R. Spronk, J. A. R. van Veen and J. C. Mol, *J. Catal.*, 1993, **144**, 472–483.
- T. Oikawa, T. Ookoshi, T. Tanaka, T. Yamamoto and M. Onaka, *Microporous and Mesoporous Materials*, 2004, **74**, 93–103.
- Otherwise, heterogeneous catalysts for the metathesis of olefins were deactivated by moisture and traces of oxygen (ref. 1).
- The visual inspection of the mixture **1a**/CO₂ was possible thanks to sapphire windows fixed on both head and bottom covers of the autoclave (see Experimental).
- <http://webbook.nist.gov>.
- It was not advisable (and also particularly difficult) to perform the activation step directly in the autoclave. Possible thermal shocks due to a rapid heating (at 550 °C) and a subsequent cooling (at rt) of the catalyst, could be a danger for the steel reactor.
- (a) K. Weiss, W. Guthmann and M. Denzer, *J. Mol. Catal.*, 1988, **46**, 341–349; (b) T. Kawai, T. Okada and T. Ishikawa, *J. Mol. Catal.*, 1992, **76**, 249–261; (c) R. Hamitil, N. Žilková, H. Balcar and J. Čejka, *Appl. Catal. A: General*, 2006, **302**, 193–200.
- D. V. McGrath and R. H. Grubbs, *Organometallics*, 1994, **13**, 224–235.
- All reactions of Scheme 2 were formal equilibria whose reversibility depended on the availability of reactant olefins, and consequently, on the reaction conditions. It should be noted that beyond 7-tetradecene, the self-metathesis of 1-octene also yielded ethylene. Likewise, the formation of olefins C₉–C₁₃ was accompanied by lower alkenes C₃–C₅. These volatile compounds however, were not observed by GC-MS.
- (a) It should be noted that the Re₂O₇/γ-Al₂O₃ system is the choice also for industrial applications of the olefin metathesis see: P. Amigues, Y. Chauvin, D. Commereuc, C. C. Lai, Y. H. Liu and J. M. Pan, *Hydroc. Process*, 1990, **69**(10), 79–80; (b) J. C. Mol, *J. Mol. Catal. A: Chemical*, 2004, **213**, 39–45. The sustainability of these large-scale processes imposes that catalysts must be recyclable.
- Chemical Synthesis Using Supercritical Fluids*, P. G. Jessop, W. Leitner, Eds.; Wiley-VCH, Weinheim, 1999; Chapt. 1.
- No improvements were observed when a freshly distilled or a brand new package (ACS grade) of *n*-heptane were used.

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- 29 It should be noted however, that the total pressure in the autoclave is almost exclusively determined by the amount of CO₂.
- 30 A. K. Coverdale, P. F. Dearing and A. Ellison, *J. Chem. Soc. Chem. Commun.*, 1983, 567–568.
- 31 J. C. Mol, *Catal. Today*, 1999, **51**, 289–299.
- 32 (a) X. Yide, H. Jiasheng, L. Zhiying and G. Xiexian, *J. Mol. Catal.*, 1991, **65**, 275–285; (b) G. Busca, *Phys. Chem. Chem. Phys.*, 1999, **1**, 723–736.
- 33 (a) L. G. Duquette, R. C. Cieslinski, C. W. Jung and P. E. Garrou, *J. Catal.*, 1984, **90**, 362–365; (b) J. C. Mol, *Catal. Today*, 1999, **51**, 289; (c) J. Handzlik, J. Ogonowski, J. Stoch, M. Mikołajczyk and P. Michorczyk, *App. Catal. A General*, 2006, **312**, 213–219.
- 34 R. M. Edreva-Kardjieva and A. A. Andreev, *J. Catal.*, 1986, **97**, 321–329.
- 35 Re-based heterogeneous catalysts for the metathesis of olefins may contain up to 18% (by weight) of the active metal (ref. 1).
- 36 D. D. Perrin, W. L. F. Armarego, In *Purification of Laboratory Chemicals*, 3rd Ed. Pergamon Press, 1988.
- 37 (a) P. Amingues, Y. Chauvin, D. Commereuc, C. T. Hong, C. C. Lai and Y. H. Liu, *J. Mol. Catal.*, 1991, **65**, 39–50; (b) A. Andreini, X. Xiaoding and J. C. Mol, *App. Catal.*, 1986, 31–40.
- 38 The conventional “teflon-coated” stirring bars were not compatible with the high temperature (550 °C) required for the activation of the catalyst.
- 39 The transfer of the solution was carried out with a canula needle under a pressure gradient of N₂. The inert (N₂) atmosphere was maintained by a rubber reservoir of ~ 2 L.
- 40 P. G. Jessop, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1996, **118**, 344–355.
- 41 MS spectra of both *cis* and *trans* 7-tetradecene gave a match quality of 96–97% when compared to standard products of the Wiley Library of Mass Spectral Data, 2002 (MS database software of the GC-MS instrument).
- 42 T. Hamatami, S. Matsubara, H. Matsuda and M. Schlosser, *Tetrahedron*, 1988, **44**, 2875–2881.