

Self-Metathesis of 1-Octene Using Alumina-Supported Re_2O_7 in Supercritical CO_2

Massimo Fabris · Cindy Aquino · Antony J. Ward ·
Alvise Perosa · Thomas Maschmeyer ·
Maurizio Selva

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Abstract In this contribution we describe the use of heterogeneous catalysts for the liquid-phase self-metathesis of 1-octene in supercritical CO_2 . Our work aims at addressing the mass-transfer problems associated with such reaction systems. By coupling a heterogeneous supported Re_2O_7 catalyst with the use of scCO_2 , the self-metathesis of 1-octene takes place by and large much more rapidly than in traditional solvent media, and furthermore, by using scCO_2 the overall efficiency and sustainability of the transformation can be improved.

Keywords Metathesis · 1-Octene · Supercritical CO_2 · $\text{Re}/\text{Al}_2\text{O}_3$

1 Introduction

The metathesis of olefins is a very elegant and widely studied reaction, in particular after the spectacular advancements obtained in the past 30 years that culminated in the Nobel Prize awarded to Chauvin, Grubbs, and Schrock in 2005. The Academy states "...[Metathesis] represents a great step forward for "green chemistry", reducing potentially hazardous waste through smarter production. Metathesis is an example of how important

basic science has been applied for the benefit of man, society and the environment".¹ Their contribution was recognized for understanding the mechanism, and for developing very efficient and selective discrete metal-based catalysts.

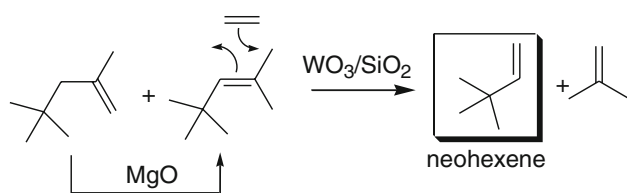
Nonetheless, one should not forget that the metathesis reaction using heterogeneous catalysis has been an established industrial process since 1966, based on the use of supported (usually on silica and alumina) metal oxides such as tungsten, nickel, cobalt, rhenium, and molybdenum. Three significant examples come to mind and are here recalled briefly. [1].

1. The historic Phillips triolefin process for the production of ethene and 2-butene from propene using a WO_3/SiO_2 catalyst, [2] that was shut down in 1972 after 6 years of operation due to increased demand for propene, and later reutilized in the reverse direction to produce propene.
2. Another industrial example by Phillips Petroleum Co. is the production of 3,3-dimethyl-1-butene (neohexene: an intermediate for musk) from ethene and a mixture of 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene (the latter is isomerised in-situ with MgO , Scheme 1) [3].
3. A large-scale industrial metathesis process is the shell higher olefin process (SHOP) for the production of C_{11} – C_{14} olefins, en route to detergents [4]. Ethene is first oligomerized to a mixture of C_4 – C_{40} alkenes, these are then fractionally distilled to isolate the C_6 – C_{18} fraction comprised almost entirely of terminal alkenes. These are then further fractionated to obtain individual α -olefins. The lighter ($<\text{C}_6$) and heavier ($>\text{C}_{18}$) alkenes

M. Fabris · A. Perosa · M. Selva (✉)
Dipartimento di Scienze Ambientali, Università Ca' Foscari,
Dorsoduro, 2137–30123 Venezia, Italy
e-mail: selva@unive.it

C. Aquino · A. J. Ward · T. Maschmeyer (✉)
Laboratory for Advanced Catalysis and Sustainability,
School of Chemistry, University of Sydney, 2006 Sydney,
NSW, Australia
e-mail: th.maschmeyer@chem.usyd.edu.au

¹ <http://www.kva.se/>



Scheme 1 The neohexene process

are subsequently isomerised to the corresponding mixture of internal olefins. The third stage involves metathesis of this mixture that produces a statistical distribution of linear internal alkenes. Distillation yields the desired fraction of C_{11} – C_{14} olefins (10–15% yield per-pass, on a scale of over one million tons per year) [5] which are then converted into detergent alcohols via hydroformylation. The remaining $<C_{10}$ and $>C_{15}$ fractions are recycled (Scheme 2).

Other industrial examples of the metathesis reaction involve mainly heterogeneous catalysis for the transformation of hydrocarbon feedstocks into olefins used in numerous applications: additives for gasoline, plasticizers, lubricants, surfactants, intermediates for detergents, polymer monomers and cross-linking agents, fragrances, pharmaceuticals, and agrochemicals [1].

As far as heterogeneous catalysis is concerned, most of the research over the past 20 years has focussed on Re supported on refractory materials such as alumina and—to a lesser extent—silica. [6] Metals such as Mo and Ru have also been supported [7] or immobilized [8, 9] on solid supports and used for the metathesis reaction, as have bimetallic Mo–W ones. [10].

While many of the earlier publications relate to gas-phase processes, where the olefins were passed through a catalyst bed, applications of the heterogeneous reaction system have been widened to the liquid-phase metathesis, involving liquid olefins such as among others: pentene, [7] α,ω -olefins, [11] unsaturated nitriles, [12] octane [10, 13, 14] and oleochemicals [15–17]. In most cases the heterogeneous catalysts required activation, e.g. by the use of organo-tin compounds.

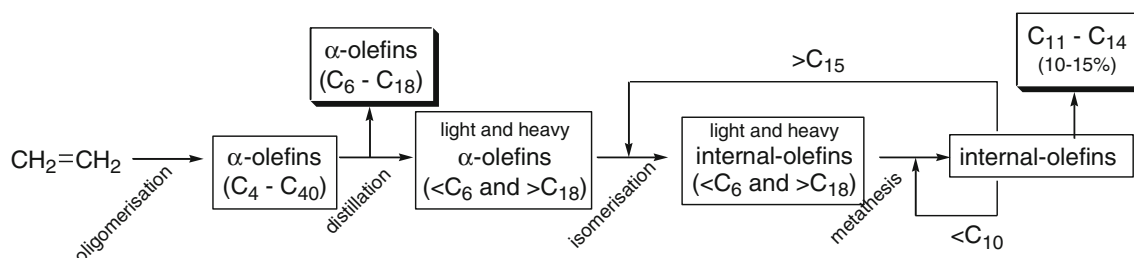
In this context one of the limitations of using solid catalyst for the liquid-phase metathesis reaction is mass transfer.

A strategy to overcome this drawback is to use supercritical carbon dioxide ($scCO_2$) as the solvent. This approach has only a few precedents which all occur in homogeneous metathesis reactions. The first is on polymerization in $scCO_2$ carried out using mainly Ru precursors, [18] and the other two deal with ring-closing-metathesis using Ru and Mo complexes [19, 20]. The ring-opening-metathesis polymerization and the ring-closing-metathesis in $scCO_2$ using well-accessible alkylidene complexes of Mo and Ru have also been reported [21]. The advantage in this case lies in the ease of isolation of the products and in the possibility of carrying out the supercritical fluid extraction.

2 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 [22]. Ammonium perrhenate ($NH_4ReO_4 \geq 99\%$) was from Aldrich. $\gamma-Al_2O_3$ was from two different sources: Puralox-Condea and Alfa-Aesar.

Catalysts Re-A₁, Re-A₂, Re-A₃, Re-A₄ and Re-S were prepared by a wet-impregnation technique described in the literature [23, 24]. A 25-mL round bottomed flask was charged with an aqueous solution (1.7×10^{-1} M, 12 mL) of NH_4ReO_4 (555 mg, 2.1 mmol) and with the chosen support ($\gamma-Al_2O_3$ or silica; 5 g). The slurry was kept under magnetic stirring for 1 h at rt, and then dried under vacuum (50 °C, 36 mbar). The solid residue was further wet with water (8 mL), stirred for 15 min at rt, and finally, dried again to the bone (50 °C, 2 mbar). The solid sample was calcined at 550 °C (10 °C/min), for 4 h, in a stream of dried air (~ 80 mL/min). All catalytic systems were characterized by optical ICP and TEM. The Re content (ICP analyses) ranged from 6.4 to 11.8%.



Scheme 2 Shell's higher olefin process

Si:Al-TUD-1 was prepared according to the previously published method [25, 26].

2.1 Synthesis of Sol–Gel Re–SiO₂ (Re-A₆)

A solution of ammonium perrhenate (0.62 g, 2.32 mmol), water (45 mL) and triethanolamine (15 mL, 0.11 mol) was stirred until the solution was homogeneous. To the resulting solution was added tetraethoxysilane (50 mL, 0.22 mol) over 10 min with stirring. After this time triethanolamine (15 mL, 0.11 mol) and tetraethylammonium hydroxide (20 wt%, 48.6 g, 66 mmol) were added. The resulting solution was then stirred for 2 h then left to stab for 24 h. The resulting viscous solution was then dried at 98 °C for 24 h. The template was then removed from the resulting solid by extraction with ethanol in a Soxhlet extractor. The product was then calcined at 600 °C for 10 h under a stream of air to obtain a white powder. Nitrogen adsorption–desorption isotherms at 77 K revealed a BET surface area of 696 m² g⁻¹, a single-point pore volume of 0.516 cm³ g⁻¹, and an average pre width of 34.2 Å.

2.1.1 The Metathesis of 1-Octene

In a typical procedure, the catalyst (Re₂O₇ supported on γ -Al₂O₃ or on SiO₂: 0.56 g, 7%) was activated at 550 °C, in dried N₂ (50 mL/min), for 1.5 h. Then, it was conveyed in a 30-mL stainless steel autoclave which was previously charged with the reactant olefin (1-octene, 0.56 g, 5 mmol). The reactor was pressurized with CO₂ by a syringe pump (ISCO 260D), and then electrically heated at 35 °C. A final pressure of 90 bar was reached. The reaction was allowed to proceed for 2 h, and the final mixture was analysed by GC/MS.

The same reactions was also carried out using conventional solvents: in this case, both the catalyst activation (550 °C, 1.5 h, N₂) and the reaction step (35 °C, ambient

pressure) took place in a standard glass flask. A solution of 1-octene (5 mmol) in *n*-heptane or toluene (the mole fraction of 1-octene was of 1.1×10^{-2}) was used.

Since heterogeneous catalysts for the metathesis of alkenes were extremely sensitive to air and humidity, all operations required a strictly inert atmosphere.

The self-metathesis product (7-tetradecene) was isolated by filtration of the catalyst and removal of the unreacted 1-octene under vacuum. The oily residue was characterized as such: the structure of 7-tetradecene was assigned by ¹H NMR and by comparison to an authentic sample.

3 Results and Discussion

3.1 Catalyst Preparation

The active catalyst for the metathesis reaction was Re₂O₇ supported on different refractory materials based on alumina. Catalysts are shown in Table 1. All but one of these materials were prepared by impregnation, [26, 27] using commercial ammonium perrhenate (NH₄ReO₄) as the precursor of the active phase. One catalyst (Re-A₆) was prepared by the sol–gel technique using the same precursor whereby the perrhenate was introduced into the template solution prior to addition of the silica source, resulting in the incorporation of the rhenium species into the silica matrix. Each sample was calcined in dry air at 550 °C, and immediately before use, activated in dry N₂ at the same temperature. Six different catalytic materials were synthesised. The final metal content (by weight) was determined by optical ICP, and it ranged from 5.5 to 7% for the alumina samples, while the sol–gel Re–SiO₂ had a value of 2.8 wt%. The catalysts on γ -Al₂O₃ (Re-A₁, Re-A₂, Re-A₃ and Re-A₄), the Si:Al-TUD-1, and the sol–gel Re–SiO₂ were characterised by TEM.

Table 1 Alumina-supported Re₂O₇ catalysts

Entry	Re wt% ^a	Support			Cat. Label	Particle size (nm) ^c
		Type	A _S (m ² /g) ^b	Source		
1	6.8	γ -Al ₂ O ₃	257	Puralox-Condea	Re-A ₁	<1
2	7.0	γ -Al ₂ O ₃	200	Alfa-Aesar	Re-A ₂	<1
3	6.4	γ -Al ₂ O ₃	257	Puralox-Condea	Re-A ₃	<1
4	11.8	Mesoporous Al ₂ O ₃	362	Ref. [27]	Re-A ₄	<1
5	7.7	Si:Al-TUD-1 ^d	298	Ref. [24]	Re-A ₅	<1
6	2.7	Sol–gel Re–SiO ₂	696	This work	Re-A ₆	<1

^a The metal content was determined by optical ICP

^b Surface area of the support. (Typically, the A_S for metathesis catalysts is ≥ 200 m²/g; Ref. [1])

^c Determined by TEM

^d Si:Al = 1:3.35

Scheme 3 Products obtained from the self-metathesis of 1-octene

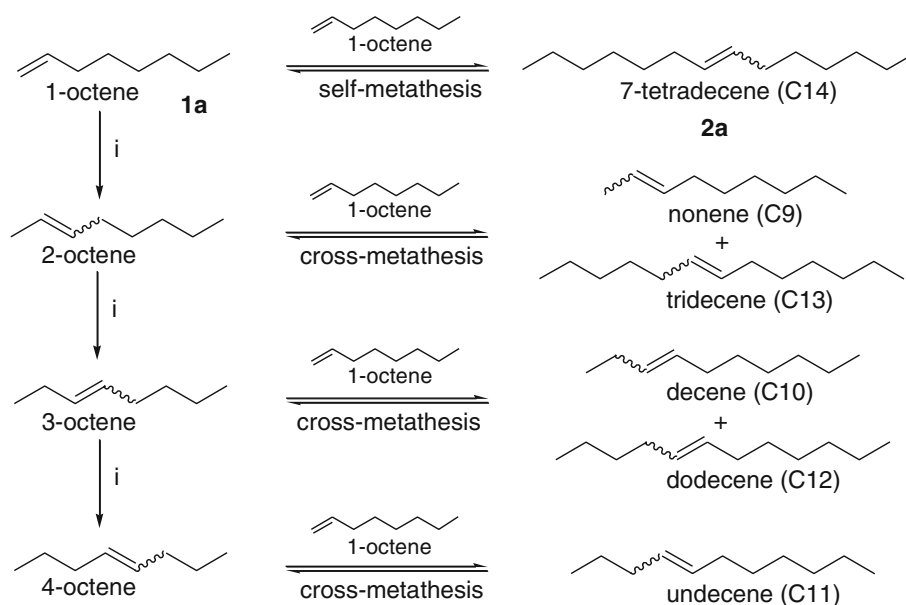


Table 2 [20] The comparison of the self-metathesis of 1-octene carried out in scCO_2 (90 bar) and in n -heptane solvents^a

Entry	Solvent	X_A ($\times 10^{-2}$) ^b (mol:mol)	Conv. (%) ^c	Products (% GC) ^c			Sel. (%) ^c
				iso	C ₉ -C ₁₃	2a	
1	scCO_2^d	1.1	74	1	2	71	96
2	n -heptane	1.1	38	1	1	36	95
3	n -heptane	1.1	42	1	1	40	95

^a All reactions were carried out for 2 hours, at 35°C, in presence of Re-A₁ as the catalyst

^b The mole fraction of 1-octene in the 1-octene/solvent solution was kept constant to 1.1 in the three media used (scCO_2 , n -heptane and toluene)

^c The reaction conversion (% by GC) was referred to all metathesis (olefins C₉-C₁₄) and isomerization compounds (Scheme 1)

^d scCO_2 : 90 bar ($d = 0.66$ g/mL)

3.2 Self-Metathesis of 1-Octene

The reaction of 1-octene (**1a**) was carried out in scCO_2 as well as in the presence of conventional liquid solvents (n -heptane and toluene: procedure adapted from ref. [27]). Initial tests were performed with Re-A₁ as the catalyst. 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. Reactions were carried out at 90 bars where the CO_2 density (0.66 g/mL) and that of n -heptane (0.67 g/mL) are similar, and because the reagents form a homogeneous phase with the scCO_2 .² Regardless of the solvent used (scCO_2 , n -heptane and toluene), the mole fraction of 1-octene ($X_{1a} = 1.1 \times 10^{-2}$) in the 1-octene/solvent solution were kept constant. The formation of the product of self-metathesis (7-tetradecene, **2a**) was always accompanied by the formation of 1-octene isomers (2-, 3-, and

4-octene) due to the acid sites on the supports and linear C₉-C₁₃ olefins which derive from the cross-metathesis reaction between 1-octene and its isomers. (Scheme 3) [10, 28, 29].

In a previous paper [30] we have observed that alumina is the best support for Re-oxide for the metathesis of 1-octene in scCO_2 . Under these conditions, the most significant aspect was that scCO_2 could not only act as a solvent for the reaction, but it also improved the overall efficiency (Table 2) [30]. At 35 °C, the reaction proceeded with an average conversion of over 30% higher in the supercritical medium than in classical liquid solvents such as n -heptane or toluene. This result is likely ascribed to two major effects: an improvement of the mass transfer due to the gas-like diffusivity and viscosity of supercritical CO_2 , and the local density enhancements able to modify the local environment around the solute molecules in the supercritical phase [31–34]. The self-metathesis selectivity was always very high (up to 96%).

² <http://webbook.nist.gov>

Table 3 The self-metathesis of 1-octene in scCO₂ with different Re₂O₇ supported catalysts

Entry	Cat.	Conv. (%) ^a	t (h)	Products (% GC)			Selectivity (%) ^c
				iso ^b	C ₉ -C ₁₃ ^c	2a ^d	
1	Re-A ₁	74	2	1	2	71	96
2	Re-A ₂	37	2	1	2	32	86
3	Re-A ₃	71	2	1	2	68	96
4	Re-A ₄	33	2	2	3	28	84
5	Re-A ₅	<1	2	<1	-	-	-
6	Re-A ₆	<1	2	<1	-	-	-
7	Re-S	<1	2	<1	-	-	-

All reactions were carried out at 35 °C, using 1-octene (5 mmol) and the catalyst (0.56 g) in the molar ratio olefin:Re = 23.7

^a The reaction conversion (% by GC) was referred to all metathesis (olefins C₉-C₁₄) and isomerization compounds (Scheme 2)

^b Total amount (% by GC) of isomerization by-products (2-, 3- and 4-octene)

^c Total amount (% by GC) of products of the cross-metathesis reaction (olefins C₉-C₁₃)

^d Total amount (% by GC) of 7-tetradecene: geometric isomers *trans/cis* were in ratio 3.8-4.0

^e Selectivity towards the product of self-metathesis: [C₁₄ (Area %, GC)/conversion (%)] × 100

3.3 Effect of the Catalyst

Once established that the metathesis reaction over alumina supported catalysts is more efficient in scCO₂ than in *n*-heptane, the different catalytic systems were tested under the same operating conditions (cf. Table 3).

Alumina was the optimal support for Re-oxide for the metathesis of 1-octene in scCO₂. In particular, only catalysts prepared from γ -Al₂O₃ were active: catalysts Re-A₁ and Re-A₃ (Puralox alumina, A_s = 257 m²/g) proved to be the best ones, yielding, after 2 h, conversions of 74 and 71%, respectively (entries 1 and 3). The reaction conversions were slightly lower on Re-A₂ (on alumina Alfa-Aesar, A_s = 200 m²/g), while the silica-supported catalysts (Re-A₄-Re-A₆) were not active at all. Similar results were gathered also by experiments (not shown here) carried out with conventional liquid solvents: both in presence of toluene and *n*-heptane, the self-metathesis of 1-octene took place only over γ -Al₂O₃ supported catalysts, but it was impracticable over silica-based systems.

The most significant aspect deals with the nature of the supports (γ -Al₂O₃, mesoporous alumina, mesoporous silica-alumina, and Re-incorporated silica). It is generally

agreed that a monomeric tetrahedral structure of ReO₄⁻ species, is stabilized over the alumina surface: the metal centre forms three equivalent Re=O moieties and a Re-O-Al bond with an acidic OH group on the support [26, 27] [35]. Although the nature of this last interaction is not fully understood, a high surface area (A_s) of the solid alumina is crucial to increase the dispersion of the active phase and to improve the catalytic performance [6]. This reason may account for the behaviour reported in Table 3. In the presence of scCO₂ as a solvent, the Re-A₁ sample supported on a γ -Al₂O₃ of 257 m²/g, allows a higher conversion with respect to the Re-A₂ catalyst prepared on a γ -Al₂O₃ of 200 m²/g. However, definite conclusions on metal dispersion and particle size cannot be drawn. The TEM analysis of Re-A₁ and Re-A₂ 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. Oikawa et al. have reported a similar result [26, 27].

As far as the mesoporous alumina as support is concerned, the higher activity reported for mesoporous Al₂O₃ was obtained with high-surface area supports (560 m²/g) [26, 27]. In our case the mesoporous Re-A₄ catalyst (entry 4, Table 1) is not as active, and is comparable to that of Re-A₂, probably due to the surface area being not sufficiently large. In addition, the Re loading is almost double the desired ratio at 11.7 wt%, hence, the lower than expected activity may be the result of having larger nanoparticles on the surface or due to nanoparticle agglomeration under the reaction conditions.

The ReO₄⁻ supported on Si:Al-TUD-1 and inserted directly into the sol-gel matrix of the catalyst Re-A₅, showed no activity. The Si:Al-TUD-1 has a relatively low surface area, while Re-A₆ has a very large surface area and the amount of Re incorporated into the silica matrix is low (2.8 wt%) due to the method of incorporation, it is therefore likely less available on the surface. In addition the presence of SiO₂ appears detrimental to the reaction (entry 7, Table 3). Silica can possess a lower surface acidity with respect to alumina [36]. This difference is claimed to explain a general poorer activity of silica-supported Re-oxide in the metathesis of olefins [6, 14, 37]. An example is the metathesis of 1-butene which is reported to take place at temperatures not below 75° C, in presence of a Re₂O₇/SiO₂ (6%) catalyst [38]. The results of Table 3 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 presence of a relatively low metal loading (7%), a convenient olefin:Re molar ratio is in the range of 20-25. Under these conditions, in supercritical CO₂ (90 bar, 35 °C, d = 0.66 g/mL), the substrate conversion reaches an equilibrium value of ~70%, after the first 120 min of reaction.

Table 4 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)	t (h)	Conv. ^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: moles of converted olefin per moles of Re per minute

3.4 The Effect of the Catalyst Amount

In presence of scCO₂, the influence of the catalyst amount on the metathesis of 1-octene, was studied using the Re-A₃ sample (Table 1). Five 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) remained the same. Results are reported in Table 4.

The conversion increased from 39 to 71% by halving the 1a:Re molar ratio (from 47.4 to 23.7; entries 1–2). Further increments of the amount of catalyst (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). This behaviour along with the calculated turnover frequency (TOF: moles of converted olefin per moles 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 get the 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 of 64% after only 1 h, 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 good level (93–96%) reported in Tables 2–3, 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 up to 7% (by GC).

4 Conclusions

At 35 °C, in presence of supercritical carbon dioxide as the solvent (90 bar), the self-metathesis of 1-octene catalysed

by heterogeneous Re-based catalysts, takes place with an average conversion over 30% higher than in conventional solvents such as *n*-heptane and toluene. This behavior is possibly due to the increase of the mass transfer promoted by dense CO₂. The most significant influence of the catalysts, deals with the nature of their support. In presence of γ-Al₂O₃, catalytic systems are active, and their performance seem improved by the increase of 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.

The catalytic activity of the SiO₂-Al₂O₃ supported catalyst is in agreement with previously examined systems that have shown that increasing Re content results in a decrease in activity. The low reactivity of the purely siliceous Re-TUD-1 is attributable to the lower Brønsted and Lewis acidity of the supports compared to alumina. In addition, since the Re is incorporated into the silica matrix during synthesis, the amount of rhenium oxide at the surface available for reaction is lower than would be the case for the same loading achieved by impregnation.

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