Green Chemistry

PAPER

Continuous-flow alkene metathesis: the model reaction of 1-octene catalyzed by Re_2O_7/γ-Al_2O_3 with supercritical CO_2 as a carrier†

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In the presence of Re_2O_7 supported on γ-Al_2O_3, the self-metathesis of 1-octene was conveniently carried out under continuous-flow (CF) conditions using supercritical CO_2 (scCO_2) as a carrier. This investigation allowed optimization of reaction parameters, the best values of which were found to be 100 °C and 90 bar, operating at flow rates of 0.05 and 1 mL min^{-1} for 1-octene and scCO_2, respectively, the reaction proceeded with very good self-metathesis selectivity (>90%) and an average productivity of ∼0.24 mL tetradecene g_{Re}^{-1} min^{-1}. Although the catalyst was completely deactivated after the first 100–150 min of reaction, it could be recycled for (at least) five subsequent reactions without any loss of performance. The results provided incontrovertible evidence that for the investigated reaction, scCO_2 was a superior carrier with respect to conventional liquids, such as toluene or n-hexane.

Introduction

In the last 20 years, largely thanks to the pioneering work of Yves Chauvin, Robert Grubbs and Richard Schrock (2005 Chemistry Nobel Prize) towards the optimization of metal–carbene catalytic complexes,[1] olefin metathesis has progressively gained momentum as a general method for the formation of new C–C bonds. This reaction not only provides an extraordinary synthetic scope that spans from commodities and functional polymers up to high value added speciality chemicals for the pharma sector, but it has also become an established green, highly atom efficient transformation, characterized by low waste generation.[2] In this respect, a fascinating and rather new area is related to the use of lower environmental impact solvents in place of conventional media for metathesis, such as light hydrocarbons or chlorinated solvents. Original applications of biphasic systems based on ionic liquids as carrier solvents for Grubbs Ru–carbenes, have been recently reviewed by Grela et al.:[3] these systems have proven successful for a number of ring-closing/opening metathesis reactions, and they enabled greener and more cost-effective processes due to the excellent confinement and recyclability of the catalyst in the ionic liquid phase. Another

attractive eco-solvent for the metathesis of olefins is dense CO_2. This is a substantially unexplored field. Only a few papers and patents report on the combination of supercritical CO_2 (scCO_2) with either Grubbs complexes or Ru- and W-based salts, for RCM and metathesis-based polymerization reactions.[4] Compressed CO_2, however, is not only a good solvent for alkenes,[5] but due to its unique low viscosity and high diffusivity, it is perfectly suited to penetrate meso- and micro-porous supports used for solid catalysts.[6] This specific theme was recently addressed by us and we were able to demonstrate the potential of scCO_2 in the self-metathesis of terminal olefins catalyzed by heterogeneous systems such as Re-oxide (Re_2O_7) dispersed on alumina and aluminosilicates (Scheme 1).[7]

Under batch conditions, the supercritical phase improved mass transport in solid catalysts up to the point that the conversions of the reactant olefins were more than 30% greater than those achieved in common hydrocarbon solvents, such as heptane and toluene. However, because of the high sensitivity of supported Re_2O_7 to traces of oxygen or water,[8] critical issues of the static method were the challenging handling and recycling of the catalyst as well as the need for lengthy procedures to achieve good reproducibility.

In order to add value to such a use of scCO_2, we were prompted to develop other methodologies, particularly continuous-flow (CF) ones, to overcome the drawbacks of batch-type
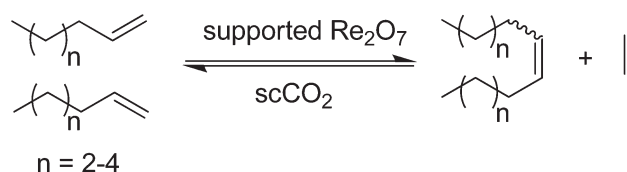
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†Electronic supplementary information (ESI) available: Details of TEM analysis and EDX spectra are reported for Re/Al$_{WI2}$ catalyst. Also, representative GC-MS spectra of some components of the oil recovered after catalyst recycling, are shown. See DOI: 10.1039/c2gc35983a

Scheme 1

n = 2-4

reactions. To the best of our knowledge, only one very recent example has been reported for the CF-metathesis of methyl oleate with compressed CO_2 as carrier.[9] This process, however, used a sophisticated SILP hybrid catalyst, *i.e.* a Ru–carbene complex immobilised on a imidazolium ionic liquid phase dispersed on silica gel, which required a careful control of process parameters to avoid leaching of the active metal phase. This paper describes an approach to alkene metathesis based on the first implementation of continuous-flow operations using $scCO_2$ as a carrier to deliver reactant and remove product olefins over a genuine heterogeneous catalytic bed of Re-oxide supported on γ-Al_2O_3(CF–$scCO_2$). CF-experiments provide evidence that: (i) $scCO_2$ is not only a vector for olefins, but, as with batch processes, it allows a superior reaction productivity compared to the usual liquid solvents (hexane and toluene); (ii) the Re-catalyst can be activated and used in a single CF-reactor without discontinuity and with minimal, if any, air/water exposure. Therefore, efficient (catalyst) recycling operations are possible; (iii) the spent catalyst after the use with liquid solvents recovers its initial performance once treated in $scCO_2$. The reactions investigated also benefit from the typical advantages of CF-methodologies, including the optimization of the operative parameters (T, P, reagent and carrier flows) and of the reaction volumes as well as the simplification of product separation. In short, process intensification aimed at improvements of synthetic, energetic and economic efficiencies of the reaction were obtained.

Results

The catalysts

Our previous investigations of batch metathesis reactions in $scCO_2$ demonstrated that Al_2O_3, preferably in the gamma phase, was by far the most convenient support among a number of different solids, including aluminosilicates and silica.[7,10] Since the objective of this work was to prove the feasibility of alkene metathesis under CF–$scCO_2$ conditions and to compare $scCO_2$ with conventional liquid solvents, only two catalytic systems based on Re_2O_7 supported on γ-Al_2O_3 were considered. They were prepared starting from NH_4ReO_4 as the metal precursor, and commercial γ-Al_2O_3 (Alfa-Aesar). A conventional wet-impregnation technique was used to disperse the active metal phase:[10] due to available equipment, samples were prepared on a 5 g scale. The catalysts were labeled as Re/Al$_{WI1}$ and Re/Al$_{WI2}$ and characterized by TEM analysis, N_2-physisorption (BET method), and ICP-OES.

The results are reported in Table 1 (further details are in the Experimental section).

As expected, the two catalytic batches showed quite similar properties. Re/Al$_{WI1}$ was used for a preliminary screening and

for the optimization of CF-conditions, while Re/Al$_{WI2}$ was used to investigate the catalyst recycling and the effect of different solvents/carriers.

The apparatus for continuous-flow metathesis reactions

The apparatus used for this investigation was assembled in-house according to Scheme 2. Three pumps (a, b, and c) delivered liquids and $scCO_2$ through the system. In particular, two twin HPLC pumps (a and b) were used for neat liquid reagents (1-olefins), and liquid solvents when necessary, while a dual-head pump with Peltier cooling device (c) conveyed CO_2 in its supercritical state. A mixture of the reactant olefin in $scCO_2$ (or in a liquid solvent) was first sent to a stainless-steel premixing cylindrical chamber (d: $L \times D = 65 \times 3.75$ mm, inner volume of 0.7 cm^3 filled with glass wool) heated at the desired reaction temperature, and then, to a stainless-steel tubular reactor (e: 150×3.75 mm, inner volume of 1.67 cm^3 filled with the catalyst). The back pressure regulator (f) at the outlet of the reactor maintained a constant operating pressure throughout the reaction. Additional N_2 and air cylinders were used during the catalyst activation step (further details are given in the Experimental section).

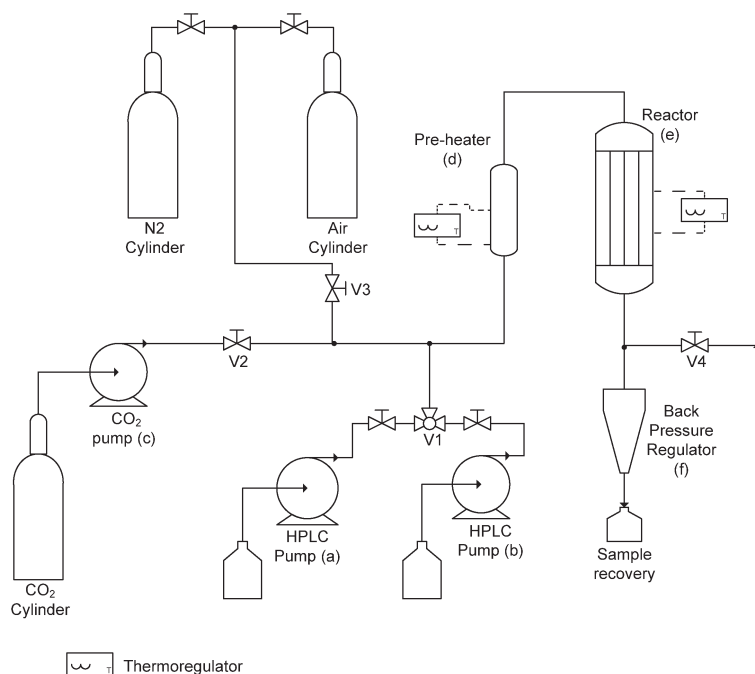### Metathesis under CF–$scCO_2$ conditions. The model self-metathesis of 1-octene

Effects of temperature, CO_2 pressure, and flow rate. 1-Octene and Re/Al$_{WI1}$ were chosen as a model olefin and catalyst to begin the study. Initial experiments were carried out to verify the suitability of the CF-apparatus, and to optimize/standardize the reaction parameters. Before each reaction, Re/Al$_{WI1}$ (1.40 g) was packed in the CF-reactor (e, Scheme 2), and activated by heating at 550 °C, first in air ($\sim$80 mL min^{-1}) for 2.5 h, and then, under a N_2 flow ($\sim$80 mL min^{-1}) for an additional 1.5 h. Once the activation was complete, the reactor was cooled down to the desired temperature and fed by a mixture of 1-octene (C$_8$) in $scCO_2$.

A first screening was performed according to the conditions used in our previous investigations on batch-CO_2 metathesis: in particular, temperature and pressure were set to 35 °C and 90 bar. Volumetric flow rates of CO_2 and of the olefin were 1.0 (F_{CO_2}) and 0.1 (F_{C_8}) mL min^{-1}, respectively. Two identical reactions were examined: at intervals, the corresponding mixtures were sampled at the reactor outlet and analyzed by GC/MS. Both experiments showed that 1-octene underwent a self-metathesis reaction to produce 7-tetradecene (C$_{14}$: mixture of *cis–trans* isomers in $\sim$1 : 4 ratio) with a very high selectivity up to 99% (Scheme 3).

Table 1 Re catalysts supported on commercial γ-Al_2O_3

| Entry	Support	Catalyst	Synthesis	Re^a (wt%)	S_A^{b} [m^2 g^{-1}]	D_p^{b} [nm]	Metal particle size^c (nm)
1	γ-Al_2O_3 (Alfa-Aesar)	Re/Al$_{WI1}$	Wet impregnation	7.1	201	6.0	0.2–0.4
2		Re/Al$_{WI2}$		6.9	206	5.9	

^{a} Re content (% by weight) determined *via* ICP-OES. ^{b} The surface area (S_A) and the mean pore diameter (D_p) were evaluated by N_2-physisorption (BET method). ^{c} Size of Re nanoparticles, from TEM analyses.

Scheme 2   The apparatus for continuous-flow metathesis.
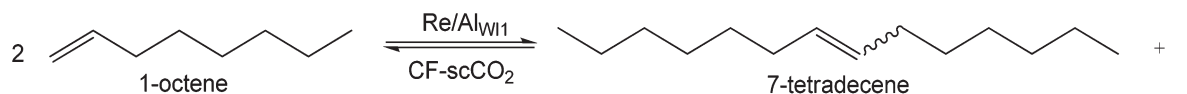
Scheme 3
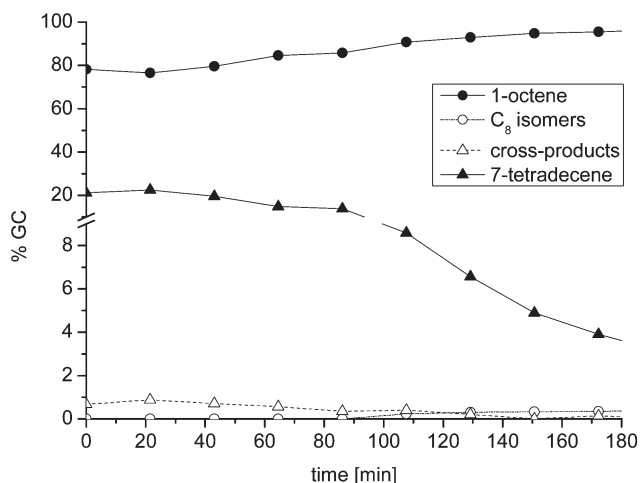
Fig. 1   The self-metathesis of 1-octene carried out at 35 °C and 90 bar under CF–scCO$_2$ conditions.

The % amounts (by GC, mean values of two experiments[11]) of reagents and products are reported in Fig. 1.

Under the explored conditions, the catalyst showed a constant activity for the first 45 min, yielding the self-metathesis product, 7-tetradecene, in a 20% yield (by GC). Then, the catalytic bed progressively deactivated to the point that, after 150 min, the

7-tetradecene amount dropped to only 5%. The structure of 7-tetradecene was assigned by its MS spectrum and it was confirmed by comparison with an authentic sample. The total amount of side-products was always very low (∼1%): they were 2-, 3-, and 4-octene and linear C$_9$–C$_{13}$ olefins that plausibly derived from the isomerization of the starting olefin and from the cross-metathesis of 1-octene and its isomers (C$_8$-isomers and cross-products; dashed lines). This product distribution matched our previous findings for the same reaction carried out under batch-CO$_2$ systems.[7,10]

Although preliminary, these results proved that unprecedented reaction conditions obtained by the combination of a CF–scCO$_2$ reactor with Al$_2$O$_3$-supported Re$_2$O$_7$ catalysts, were suitable for metathesis processes.

To investigate the effect of temperature and pressure on the CF–scCO$_2$ self-metathesis of 1-octene, two sets (a and b) of experiments were performed. In the first set (a), five reactions were carried out at 35, 100, 110, 120 and 150 °C, at a constant CO$_2$ pressure of 90 bar; in the second one (b), four reactions were followed at 100 °C by setting the pressure at 60, 90, 110, and 150 bar. In all cases, the catalyst was Re/Al$_{WI1}$ and the volumetric flow rates were 1.0 mL min^{-1} for CO$_2$ (F_{CO_2}), and 0.1 mL min^{-1} for 1-octene (F_{C_8}). Based on the results of Fig. 1, mixtures were sampled at the reactor outflow after the first 15 min of each reaction, and then, analyzed by GC/MS. Fig. 2a and 2b illustrate the conversion of 1-octene and the product distribution as a function of the temperature and the pressure.
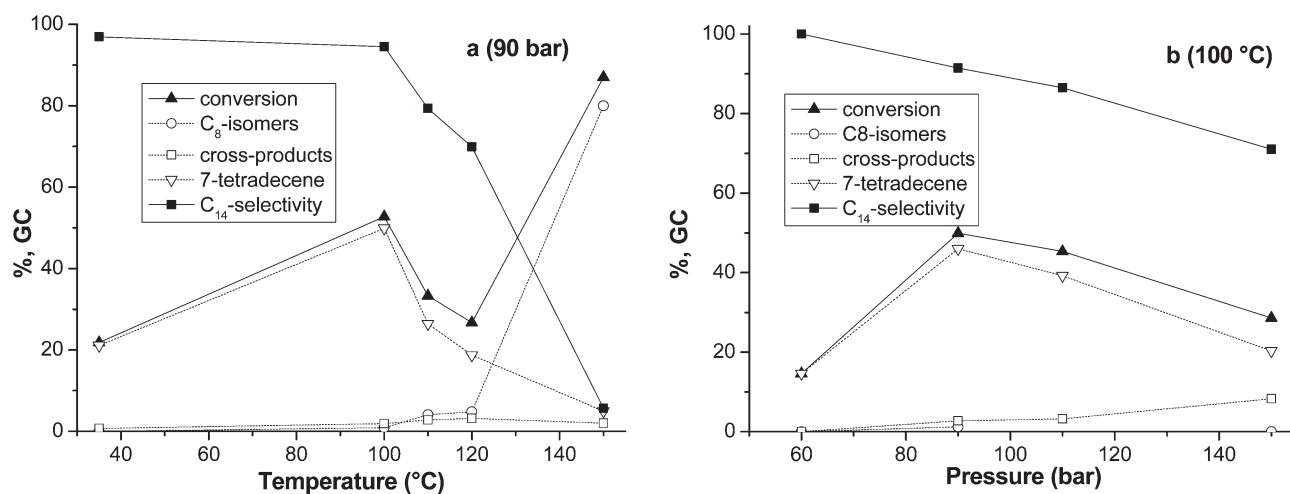
Fig. 2 The self-metathesis of 1-octene under CF–scCO$_2$ conditions: conversion and product distribution after the first 15 min. (a) The effect of the reaction temperature; (b) the effect of the CO$_2$ pressure.

Temperature (Fig. 2a)

The increase of the temperature from 35 to 100 °C improved the conversion of 1-octene from 23 to 51%, with no appreciable effects on the selectivity towards 7-tetradecene, which always remained very high (>95%). However, a further enhancement of the temperature to 110–120 °C had detrimental consequences: the conversion of 1-octene dropped to 27%, and, at the same time, the formation of C$_8$-isomers and cross-metathesis products was favored over the desired self-metathesis reaction. Finally, at 150 °C, the isomerization of the starting alkene became the major (if not exclusive) transformation. Under such conditions, the reaction conversion was substantially quantitative, but the amount of 7-tetradecene was less than 5% of the total detected products.

CO$_2$ pressure (Fig. 2b)

The transition of CO$_2$ from the subcritical vapor at 60 bar (ρ_{CO2} = 0.099 g mL^{-1},[12]) to the supercritical phase at 90 bar (ρ_{CO_2} = 0.16 g mL^{-1},[12]) came with a significant increase of the conversion of 1-octene that tripled from 15% to 50%. At the same time a very moderate decrease of the self-metathesis selectivity was observed (from 99% to 93%). However, if the CO$_2$ pressure was further increased to 110 and 150 bar (ρ_{CO_2} = 0.21 and 0.33 g mL^{-1}, respectively[12]), the conversion progressively dropped to 28%, and the amount of cross-metathesis by-products went up to 8%.

Flow rate of 1-octene

Under the optimal conditions of temperature and pressure identified by the previous experiments (100 °C and 90 bar, respectively), three experiments were run by setting the volumetric flow rate of the reactant 1-octene (F_{C_8}) at 0.05, 0.1 and 0.5 mL min^{-1}, respectively. The flow rate of CO$_2$ (F_{CO_2}) was kept constant at 1.0 mL min^{-1}. Fig. 3 reports the composition of the mixtures
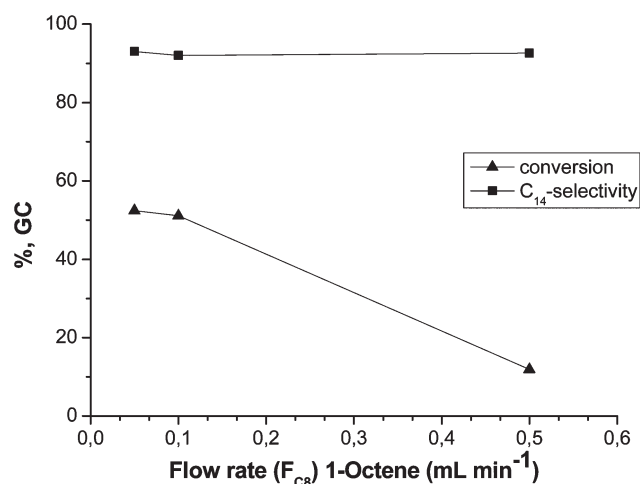

Fig. 3 The effect of the volumetric flow rate of 1-octene on the reaction conversion and the selectivity towards 7-tetredecene, for the CF–scCO$_2$ self-metathesis of 1-octene.

sampled at the reactor outflow, after the first 15 min of each reaction, vs. F_{C_8}.

The conversion of 1-octene was substantially steady at ~50% in the range of lower flow rates (0.05–0.1 mL min^{-1}), while it underwent a significant decrease from ~50 to 12%, when the flow of the starting alkene was ten-fold increased from 0.05 to 0.5 mL min^{-1}. Regardless of these variations, the self-metathesis selectivity always remained very high at 92–94%.

The reactivation of the catalyst and the reproducibility of the reaction. The optimization of temperature, pressure, and flow rate for the metathesis of 1-octene (Fig. 2 and 3) not only confirmed the feasibility of the reaction under CF–scCO$_2$ conditions, but it offered a basis for the investigation of other crucial aspects. These included: (i) the reactivation/reuse of the catalyst and the reproducibility of the procedure, which were both very
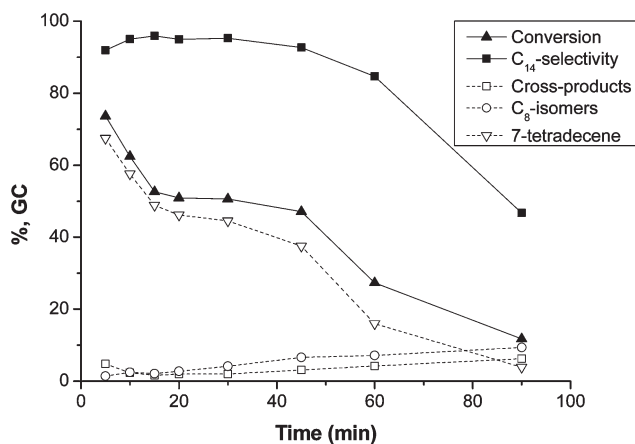
Fig. 4 The self-metathesis of 1-octene on Re/Al_{WI2} under $CF\text{-}scCO_2$ conditions (100 °C and 90 bar CO_2 and 1-octene at 1.0 and 0.05 mL min^{-1}). C_{14}-Selectivity: selectivity towards 7-tetradecene (the self-metathesis product).

Fig. 5 The self-metathesis of 1-octene under $CF\text{–}scCO_2$ conditions: recycling of the Re/Al_{WI2} catalyst.

problematic in batch-CO_2 systems, and (ii) the comparison of $scCO_2$ with conventional liquid solvents in the CF-mode.

Accordingly, T, P, and F were set at 100 °C, 90 bar, and 1.0 mL min^{-1} for CO_2 and 0.05 mL min^{-1} for 1-octene.[13] Re/Al_{WI2} (1.4 g) was used as the catalyst for this study.

Fig. 4 exemplifies the result achieved using this set of parameters and the new catalyst batch. The behavior resembled that of Fig. 1: during the first 45 min of the reaction, a steady conversion of 1-octene was reached with a very high selectivity towards self-metathesis (C_{14}-selectivity > 95%, solid profiles). With respect to Fig. 1, however, the higher temperature allowed a higher conversion (~50%) and a better average productivity (~0.24 mL tetradecene g_{Re}^{-1} min^{-1}). After 90 min, the catalyst was substantially deactivated and the corresponding conversion and C_{14}-selectivity dropped to 12% and 46%, respectively. The residual products derived mainly from the isomerization of the starting alkene (to 2-, 3-, and 4-octene, respectively), and from the cross-metathesis of 1-octene and of its isomers (dashed bottom lines).

It should also be noted that both self- and cross-metathesis reactions were formal equilibria where the formation of 7-tetradecene and olefins C_9–C_{13} was accompanied also by ethylene (Scheme 3) and lower alkenes C_3–C_5 (not detected by GC-MS), respectively. Since these volatile compounds could not be released under our conditions, the investigated reactions could not go to completion. The equilibrium position was clearly identified for batch metathesis in $scCO_2$;[7] the same, however, was less accurate for the corresponding CF-processes.

At the end of the reaction detailed in Fig. 4, reactivation and reuse of the catalyst was explored. After 120 min, the flows of both CO_2 and 1-octene were stopped and the catalytic bed was first washed with acetone (1.5 mL min^{-1}; 20 min) and then with $scCO_2$ (1 mL min^{-1}; 10 min) at 80 °C. The catalyst was subsequently activated using the above described procedure (550 °C: air: ~80 mL min^{-1}, 2.5 h; N_2: ~80 mL min^{-1}, 1.5 h), and re-used for the metathesis of 1-octene (100 °C, 90 bar; CO_2 and 1-octene at 1.0 and 0.05 mL min^{-1}, respectively). A total of five cycles of activation and reaction were carried out. The results are reported in Fig. 5: both the conversion of 1-octene
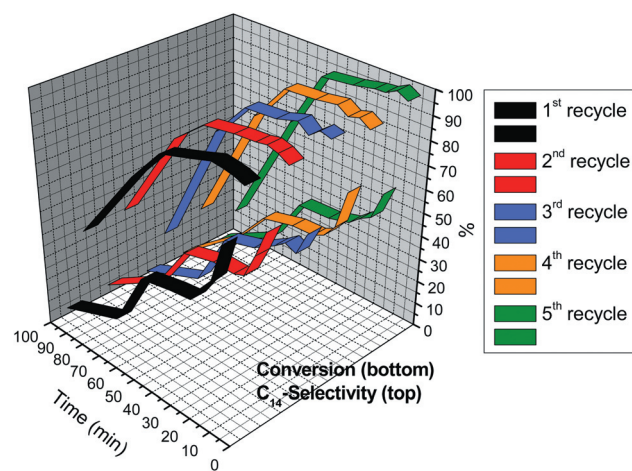
and the C_{14}-selectivity (bottom and top profiles, respectively) are grouped by colors for each of the five subsequent experiments.

Reaction profiles not only showed a reasonably good overlap from one experiment to another, but they corroborated the trend of Fig. 4. In particular, conversions and C_{14}-selectivity reached steady values (in the range of 45–50% and 90–95%, respectively) in the time interval from 15 to 45 min; then, they dropped to 9–12% and 25–40%, respectively, after 90 min.

Once the last (fifth) recycle was complete, the catalyst was washed with acetone/$scCO_2$ *via* the procedure described above. The recovered liquid effluent was rotary-evaporated yielding a very small amount of a viscous oil (<40 mg) the GC/MS analysis of which suggested the presence of hydrocarbon-like structures with molecular weights ≥300 (see ESI† section for details). The catalytic bed was then discharged from the reactor and dried under vacuum overnight. The weight of the spent solid showed no appreciable variation with respect to that of the starting catalyst (1.40 g). Overall, the formation of carbonaceous residues and/or other heavy by-products could be substantially ruled out during our metathesis experiments.

To get further insight into the catalyst behavior, TEM analyses and N_2-physisorption measures were carried out on both the fresh and the spent Re/Al_{WI2} solid (after five recycles). The results are reported in Table 2 and Fig. 6 and 7.

Except for moderate variations of the surface area and pore diameter, the metal/support structure of the fresh system did not

Table 2 Properties of Re/Al_{WI2} before and after its use for the metathesis of 1-octene

Entry	Catalyst Re/Al_{WI2}	S_A[b] [m²/g]	D_p[b] [nm]	Metal particle size[c] (nm)
1	Fresh	206	5.9	0.2–0.4
2	Spent[a]	167	6.9	0.2–0.5

[a] After five subsequent reactions of self-metathesis of 1-octene under CF–$scCO_2$ conditions (Fig. 5). [b] The surface area (S_A) and the mean pore diameter (D_p) were evaluated by N_2-physisorption (BET method on desorption isotherms). [c] Size of Re particles, from TEM analyses.
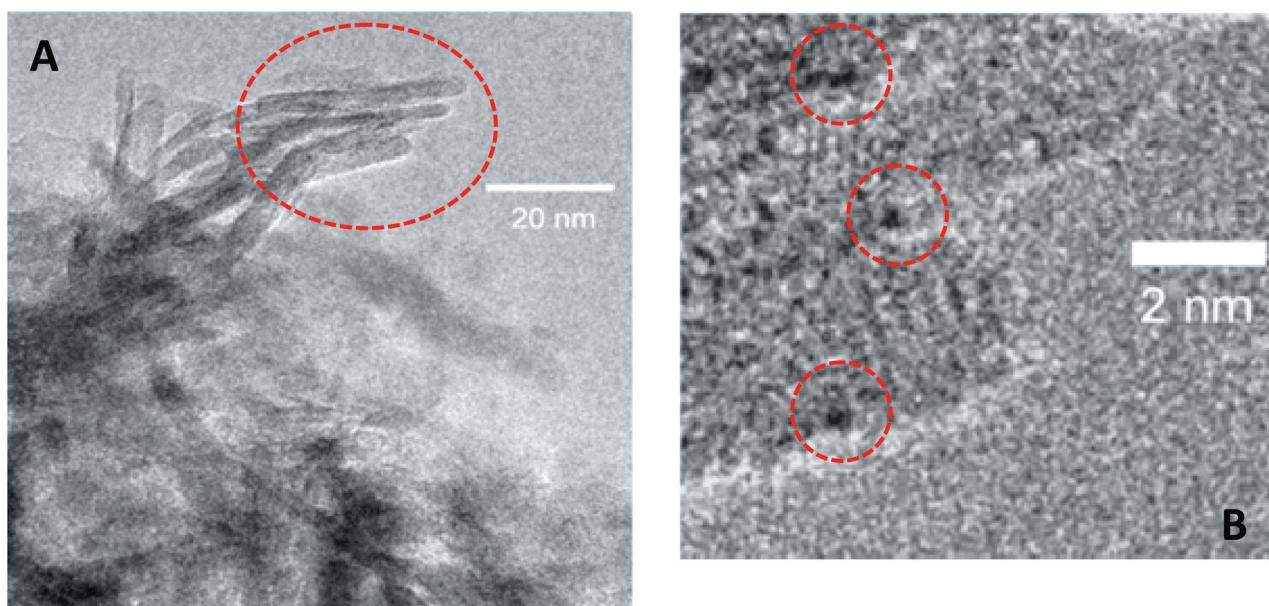
Fig. 6 TEM images of the fresh catalyst. A: the morphology of γ-Al$_2$O$_3$ support. B: the supported metal (Re).
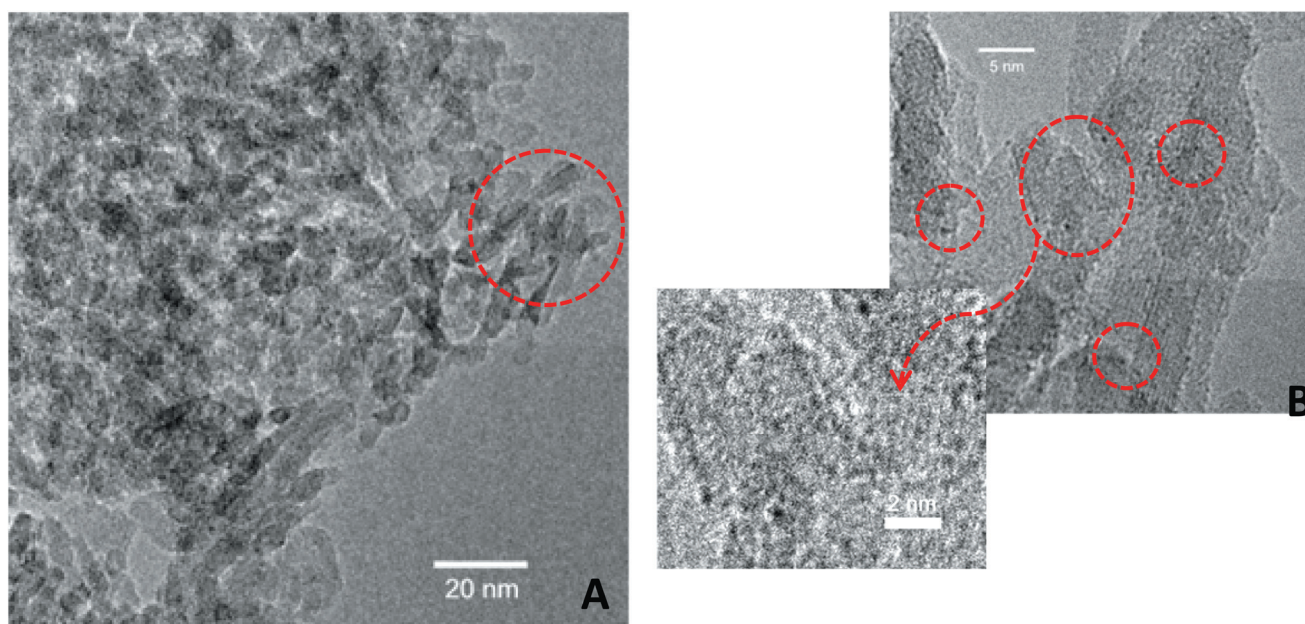
Fig. 7 TEM images of the spent catalyst. A: the morphology of γ-Al$_2$O$_3$ support. B: the supported metal (Re).

vary with respect to the spent one. In particular, from TEM measurements:

Fig. 6A of the fresh catalyst showed the presence of acicular-shaped well-organized crystals of γ-Al$_2$O$_3$ (the needle average size was in the range of 15–30 nm). The enlargement indicated the presence of 2–4 Å Re nanoparticles (Fig. 6B).

Fig. 7A of the spent catalyst showed that, after the reaction, the morphology of γ-Al$_2$O$_3$ was only partly preserved: the oxide was still in a highly crystalline form, but its original acicular structure was, to some degree, lost. The enlargement proved that the average size of Re particles was 2–5 Å (Fig. 7B), *i.e.* in the

same range of the fresh catalyst. Sintering phenomena of the supported metal could therefore be ruled out.

In both the fresh and the spent catalyst, the presence of sup-ported-Re was confirmed also by energy dispersive X-ray (EDX) analyses. The corresponding spectra showed typical signals of Re, along with Al and O of the oxide framework (see ESI† section, for further details).

These results ultimately proved that: (i) CF–scCO$_2$ conditions allowed a good reproducibility. Re-oxide on γ-alumina was a robust catalyst that could be recycled up to five times without any substantial loss of its activity; (ii) no formation/retention of

high molecular weight side-compounds occurred on the active metal phase.

Comparison of scCO₂ with conventional liquid solvents under CF-conditions. The performance of $scCO_2$ as a solvent for the CF-metathesis of 1-octene, was compared to that of organic liquids, such as *n*-hexane and toluene, both conventionally used as reaction media for the same reaction. Experiments were carried out under the conditions of Fig. 4, in the presence of Re/Al$_{WI2}$ as the catalyst. To allow for a meaningful comparison, solutions of 1-octene in both *n*-hexane and toluene were prepared and set to react at the same molar fraction used for solutions of 1-octene in $scCO_2$.[14] 1-Octene was fed to the reactor at 0.05 mL min⁻¹, while flow rates of *n*-hexane and toluene were 2.98 and 2.45 mL min⁻¹, respectively. Reactions were carried out at 100 °C and at 90 bar in all cases. Results are reported in Fig. 8. Profiles of conversion (dashed blue and red lines) and C₁₄-selectivity (solid blue and red lines) are illustrated for reactions in *n*-hexane and toluene solvents, respectively. For convenience, the corresponding results in $scCO_2$ are also shown (black profiles).

Comparable behaviors were observed for reactions performed in the presence of *n*-hexane and toluene. Initial conversions and C₁₄-selectivity were similar to those observed in $scCO_2$ (~65% and 90%: respectively, blue and red profiles). However, with *n*-hexane and toluene, the catalytic bed abruptly deactivated to become completely inefficient for the metathesis in less than 15 and 30 min, respectively (solid red and blue lines). From those times on, the C₁₄-selectivity dropped to zero and the residual conversions were due only to isomerisation side-reactions of the starting alkene. This behavior left few doubts about the superior capability of $scCO_2$ (black profiles) as a carrier for the investigated reaction.

Further experiments also demonstrated that after the reaction with liquid solvents (*n*-hexane and toluene), the exhausted catalyst could recover an activity comparable to that of Fig. 4, when it (catalyst) was reused in $scCO_2$. To explore this aspect, once the reaction carried out in toluene was complete (blue profile of Fig. 8), the catalytic bed was washed (80 °C: acetone at 1.5 mL min⁻¹ for 20 min followed by $scCO_2$ at 1 mL min⁻¹ for 10 min),
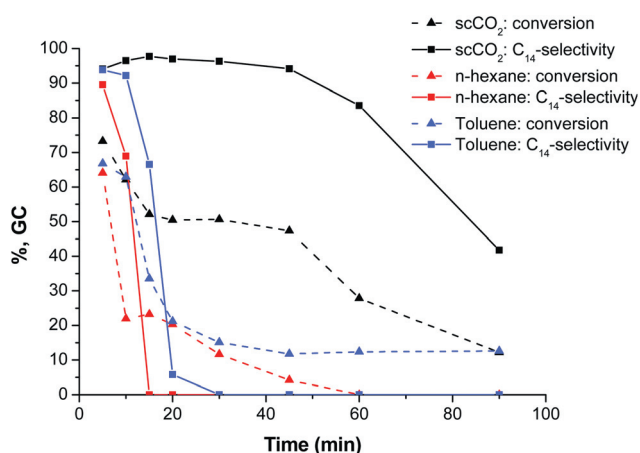
and recycled for three subsequent metathesis reactions under the CF–scCO₂ conditions of Fig. 4. Results are reported in Fig. 9 where profiles of conversion (dashed lines) and C₁₄-selectivity (solid lines) are grouped in four different colors, each of them corresponding to a single experiment (blue: toluene; fuchsia, red, and olive: 1st, 2nd, and 3rd recycles, respectively, in $scCO_2$).
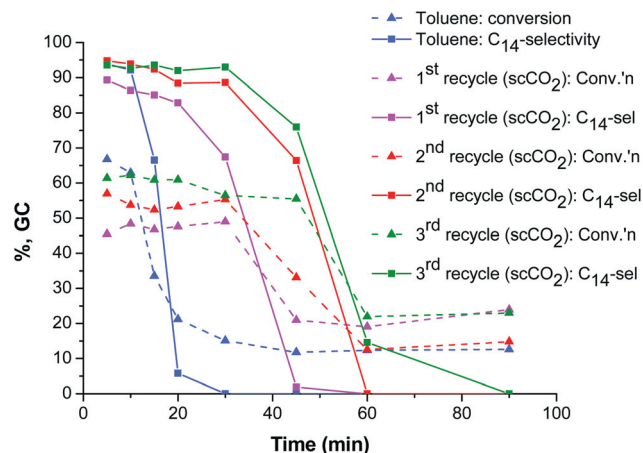
Since the first recycle in $scCO_2$, both conversion of 1-octene and self-metathesis selectivity were enhanced with respect to the reaction in toluene (compare blue and fuchsia curves). This trend continued during the reuses of the catalyst in scCO2 at the point that, after the 3rd recycle, the reaction outcome was not significantly different from that obtained with a fresh Re/Al$_{WI2}$ sample (compare Fig. 4 and 9: black and olive profiles, respectively). In other words, the remarkable deactivation observed with liquid solvents was reversible: $scCO_2$ helped to restore the catalyst performance.

Discussion

This investigation provides good evidence of the suitability of CF–scCO₂ conditions for the metathesis of alkenes catalyzed by Re-oxide supported on γ-Al₂O₃. The analysis of the effects of the main reaction parameters (*T*, *P*, and flow rate) has not only served for optimization of CF-operations, but it allows us to speculate on the behavior of the supercritical phase and on benefits of its use.

Temperature and pressure

Under isobaric conditions (90 bar), the increase of the temperature from 35 to 100 °C improves the conversion of 1-octene with no appreciable effects on the self-metathesis selectivity (>90%, Fig. 1 and 2a-left). Under isothermal conditions (100 °C), the change from 60 to 90 bar (vapor-to-supercritical CO₂) considerably favors the self-metathesis of 1-octene. The reaction, however, is disfavored by an additional increase of the CO₂ pressure up to 150 bar (Fig. 2b). Density (ρ) and viscosity (η) of

Fig. 8 The self-metathesis of 1-octene under CF-conditions: comparison of scCO₂ (black), *n*-hexane (red), and toluene (blue) as solvents. Conversion of 1-octene: dashed lines; C₁₄-selectivity: solid lines.

Fig. 9 The effect of recycling of the Re/Al$_{WI2}$ catalyst under CF–scCO₂ conditions upon the metathesis of 1-octene in toluene (blue profile).
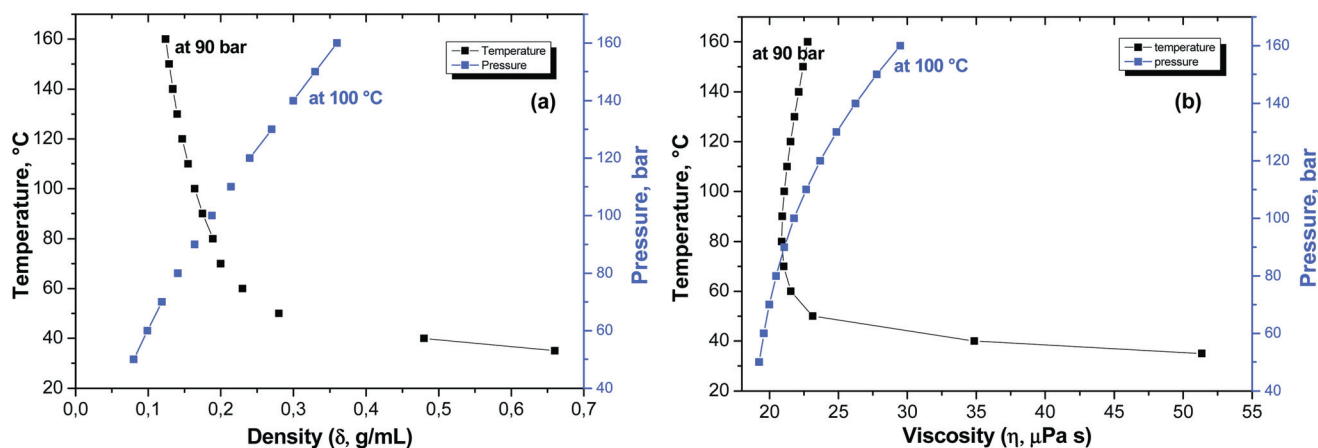
Fig. 10 (a) and (b): isobaric and isothermal trends of density (ρ, top) and viscosity (η, bottom) of pure CO_2, at 100 °C and 90 bar, respectively.

the supercritical phase may play a crucial role. Both these parameters can be tuned by variations of T and P and they are usually assumed to control the major effects induced by $scCO_2$. Fig. 10a and 10b report the isobaric and isothermal trends of ρ and η at 100 °C and 90 bar, respectively.[12] The intervals of temperatures and pressure correspond to those investigated in this work.

Isobaric profiles (black) at 90 bar show that ρ and η reach the relative highest values (0.67 g mL^{-1} and 53 µPa s, respectively) in the proximity of the supercritical temperature (35–40 °C). As the temperature increases, density and viscosity markedly decrease until 90–100 °C; then, very smooth changes are observed in the range of 100–150 °C. Instead, isothermal profiles (blue) at 100 °C show a continuous increase of both ρ and η over the whole investigated range of CO_2 pressure, from 60 to 150 bar. These trends may offer an explanation for Fig. 2a and 2b. The kinetics of the CF-metathesis is certainly favored by the temperature (up to 100 °C), but the final outcome is also determined by the optimization of the CO_2 properties. Optimal density and viscosity of the supercritical carrier was found to be around 0.15 g mL^{-1} and 20 µPa s, respectively. Under these conditions, the best compromise between moderate solvation effects and good capabilities for mass-transport of the substrate/product to and out of the catalyst is achieved.[15]

At 150 °C, however, the desired metathesis reaction is inhibited and the isomerization of the starting alkene takes over (Fig. 2a, right). This behavior is consistent with literature data reporting that at a high temperature (usually over 100 °C), metathesis catalysts, particularly $Re_2O_7/\gamma\text{-}Al_2O_3$, become efficient for C–C double bond isomerisation due to the Brønsted acid sites (*i.e.* the hydroxyl group on the catalytic surface) of the support.[16]

One last observation should remark on the role of the phase behavior, since both ρ and η as well as the critical temperature and pressure of pure CO_2 (Fig. 10) are different from those of the flowing mixture of CO_2, octene, tetradecene and ethane. Different studies have pointed out that for reactions in CO_2 solvent, below the critical point, the rate may increase with CO_2 pressure because an expanded liquid phase with higher diffusivity and lower viscosity forms.[17] This would help the contact of

liquid reagents with the catalyst. Above the critical point, however, reagents are favorably partitioned in the supercritical phase (throughout the whole reactor), so that their concentration at the catalytic bed is reduced. Consequently, the reaction rate drops. This may offer an alternative explanation for the observed pressure effect, especially for the lower conversion at higher pressure (150 bar).[18]

Flow rate

Two aspects emerge from the analysis of Fig. 3: (i) if the olefin flow-rate is doubled (from 0.05 to 0.1 mL min^{-1}), the conversion does not appreciably vary; (ii) if a ten-fold increase of the olefin flow-rate (from 0.05 to 0.5 mL min^{-1}) is applied, the conversion of 1-octene decrease to only one quarter of its initial value, from ~50 to 12%. This suggests that TOF (the rate of consumption of 1-octene per mass unit of the catalyst) may be improved by operating at higher flow rates of the reactant. However, the modest conversion per pass has limited any further optimization of residence times under the conditions investigated in this work. Studies are in progress using higher catalyst loadings in larger reactors.

Continuous-flow *vs.* batch conditions for metathesis reactions in $scCO_2$

At 35 °C and 90 bar, the maximum CF-conversion for the self-metathesis of 1-octene (23%) is far lower than that (65–70%) obtained for the same reaction in the static mode.[7,10] Also, a CO_2 pressure dependence is observed for the CF-metathesis, while the corresponding batch process is insensitive to pressure effects. The reaction environment is therefore greatly differentiated when CF-dynamic or static conditions are used. At least two aspects should be considered, including: (i) different local density enhancements (LDEs) effects due to the supercritical phase,[19] and (ii) the sensitivity of metathesis equilibria to the release of gaseous by products (ethylene and other light olefins) and to the CO_2 pressure.

Fig. 5 leaves few doubts that the CF–$scCO_2$ mode is suited to preserve the catalyst for subsequent reactions: the experimental
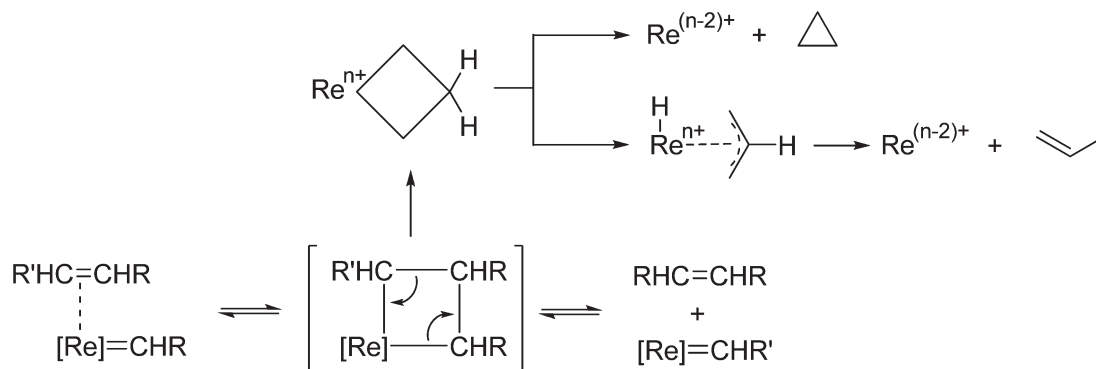
Scheme 4 Metathesis and reductive elimination on Re based catalysts.

setup allows the activation, the reaction, and the final cleaning step of the Re-supported catalyst in a single reactor with minimal air exposure.[8] This guarantees the catalyst life/performance during recycling tests under CF-conditions. This is a major advantage over static reactions for which the catalyst handling represents a critical issue.

Different solvents for CF-metathesis reactions

Because of compression costs and potential hazards of high-pressure operations, the substitution of liquid solvents with $scCO_2$ for a given reaction becomes a genuine green innovation only when $scCO_2$ contributes to improve the process productivity with respect to traditional conditions. Fig. 8 and, particularly, Fig. 9 show how this requisite is fulfilled by the CF–$scCO_2$ procedure here described for metathesis reactions. The use of $scCO_2$ not only allows us to considerably extend the catalyst life/activity in each single CF-experiment (Fig. 8), but the supercritical carrier also allows the restoration of the catalyst performance upon its use in a liquid solvent such as toluene (Fig. 9). This confirms that the deactivation of Re-oxide is somewhat reversible in the presence of $scCO_2$. The above mentioned solvation and/or mass transport phenomena likely account for the result. Whatever the effect, this represents the most convincing evidence for an advantageous use of $scCO_2$ over conventional solvents for the CF-self-metathesis of 1-octene.

Catalyst deactivation

The comparison of the properties of fresh and spent catalysts does not offer proof for the deactivation observed during the metathesis reaction. For example, after five recycles of the Re/Al$_{WI2}$ sample: (i) BET measures show a moderate decrease (17%) of the surface area from the fresh system (206 m^2 g^{-1}) to the exhausted one (167 m^2 g^{-1}; Table 2), and (ii) TEM analyses indicate no substantial modification of both the support structure and the size of Re-particles, suggesting that no sintering phenomena occur. Gravimetric determinations also indicate that the weight of the spent catalytic bed (1.40 g) does not change. However, after the catalyst washing with acetone/$scCO_2$, a minor amount of an oily residue (<40 mg per ~5 mL of reactant 1-octene) is recovered, the composition of which is consistent

with the formation of high-molecular weight hydrocarbons. These products plausibly originate from competitive oligomerisation side-reactions, which are well documented in the literature of alkene metathesis.[20] The very low-level of oligomers may account for the slow poisoning of the catalyst surface. Other considerations include the reaction mechanism. The generally accepted pathway for the metathesis reaction invokes the formation of a metal–carbene followed by a metallacyclobutane intermediate (Scheme 4, bottom).[21] In the case of rhenium oxide based catalysts, the latter species plausibly undergoes a reductive elimination, which brings the oxidation state of the active metal below its optimal value (Scheme 4, top). The ultimate consequence is an intrinsic deactivation.[22]

The comparison of different catalysts/supports would certainly help to clarify such an aspect. However, this is beyond the scope of the present work.

Conclusions

This paper describes the first reported implementation of a continuous-flow procedure for the metathesis of 1-octene using the combination of Re_2O_7/γ-Al_2O_3 as a catalyst and $scCO_2$ as a reactant/product carrier. With respect to the same reaction under static conditions, the general advantage coming from the CF-mode is the good control of the main reaction parameters (T, P, and flow rate of both reagent and carrier) that allows us to optimize the outcome in terms of conversion and selectivity, and to guarantee the reproducibility of the results. However, the most striking evidence for the potential of $scCO_2$ is seen in the comparison of the supercritical carrier to conventional liquid solvents: with respect to toluene or n-hexane, the use of $scCO_2$ considerably extends the catalyst life, and it improves and restores the catalyst performance so that efficient recycling is possible. Solvation and mass transport phenomena have been considered to explain such a result. In the range of temperature and pressure used for the CF-experiments, the analysis of the variation of both the density and the viscosity of $scCO_2$ suggests that optimal values should be around 0.15 g mL^{-1} and 20 µPa s, respectively.

A concern exists over the deactivation of the catalyst after the first 60 min of CF-exercise. A role may be played by the slow poisoning caused by build-up of oligomers as well as the

reductive elimination of a metallacyclobutane intermediate. This aspect will be the object of further studies.

Finally, only one model substrate (1-octene) has been examined, but in analogy to our previous study under static mode with CO_2 solvent, no practical limitations are foreseen for the self-metathesis of other terminal olefins in the range of C_6–C_{12} liquid compounds.

Experimental

General

1-Octene, n-hexane and toluene were ACS grade and they were used as received. Ammonium perrhenate (NH_4ReO_4, ≥99%) was from Aldrich. γ-Al_2O_3 was from Alfa-Aesar with a surface area (S_A) of 257 m^2 g^{-1}. GC-MS (70 eV) analyses were run using a FactorFour VF23 capillary column (30 m). Gaseous N_2 and air used throughout the activation of catalysts and the reaction step (see below), were R-grade. Wherever used, water was of milli-Q grade. CO_2 was SFC/SFE grade (purity 99.998%).

Preparation and characterization of catalysts

Re_2O_7/γ-Al_2O_3 catalysts were prepared by a wet-impregnation technique already reported by us.[7] Accordingly, two catalytic samples were obtained starting from NH_4ReO_4 (555 mg, 2.1 mmol) and γ-Al_2O_3 (5 g) in both cases. They were labeled as Re/Al$_{WI1}$ and Re/Al$_{WI2}$, and they were characterized by optical ICP, TEM, and N_2-physisorption. ICP and TEM analyses were carried out on samples of 50 and 20 mg, respectively, according to procedures described in our previous papers.[7,10]

(High-resolution) Transmission electron microscopy (HR-TEM) images were obtained by using a JEOL JEM 3010UHR (300 kV) TEM (point to point resolution at Scherrer defocus of 0.17 nm) fitted with a single crystal LaB6 filament and an Oxford INCA Energy TEM 200 energy dispersive X-ray (EDX) detector. All samples were dry deposited on Cu "holey" carbon grids (200 mesh).

N_2-physisorption was carried out as follows: an aliquot of the solid catalyst (150 mg) was charged in a sample tube of an automatic physisorption analyzer (Micromeritics ASAP 2010) and degassed under vacuum at 110 °C for 2 h. Specific surface area and pore size distribution were evaluated through N_2 adsorption–desorption isotherms at −196 °C: the surface area was calculated on the basis of the BET equation, whereas the pore size distribution was determined by the BJH method applied to the desorption branch of the isotherm.[23]

Major features of Re/Al$_{WI1}$ and Re/Al$_{WI2}$ catalysts were described in Tables 1 and 2.

General procedure for the metathesis of 1-octene under CF–scCO$_2$ conditions

CF–scCO$_2$ experiments for the self-metathesis of 1-octene were carried out according to the apparatus illustrated in Scheme 2.

SAFETY WARNING. Operators of high pressure equipment should take proper precautions to minimize the risk of personal injury.[24] The apparatus must be carefully checked to prevent leakage and pumps must have pressure monitors and safety devices able to prevent any overpressure.

In a typical CF–scCO$_2$ metathesis reaction, 3 operations were performed in the following order:

Preparation of the reactor and catalyst activation. The reactor (1/4″ pipe, 1.67 mL, $L \times \varnothing = 150 \times 3.75$ mm) was filled with the catalyst (1.40 g). The catalyst was placed between two layers of glass wool capped with steel frits (2 μm) at the top and the bottom of the reactor. Once filled, the reactor was fitted in the apparatus and placed in a brass heating block. The catalyst was then activated by heating it at 550 °C (at 10 °C min^{-1}) in an air flow (∼80 mL min^{-1}, 1 atm.) for 2.5 h, followed by a N_2 flow (∼80 mL min^{-1}, 1 atm.) for an additional 1.5 h. Two cartridge heaters and a thermocouple dipped in the brass heating block of the reactor allowed us to reach and check the activation temperature via a programmable controller.

Reaction and the analysis of the reaction mixture. At the reaction temperature, the back pressure regulator (BPR) was set to the operating pressure, typically 90 bar. Using valves V2 and V3, the N_2 flow was stopped and CO_2 was pumped into the system through a Jasco PU-2080-CO_2 pump (C in Scheme 2). For most experiments, the flow rate of CO_2 was set to 1.0 mL min^{-1}. After 5 min, 1-octene was also pumped through valve V1 in the same circuit of CO_2: a Shimadzu LC-10AS HPLC pump (A in Scheme 2) was used for this purpose. A typical flow rate of the olefin was 0.05 mL min^{-1}. The combined flow of olefin and scCO$_2$ went through a stainless-steel cylindrical premixing chamber (d: $L \times D = 65 \times 3.75$ mm, 0.7 mL filled in with glass wool) previously heated at the reaction temperature, and finally reached the reactor. The automated BPR controlled by an internal pressure transducer ensured that the operating pressure was kept constant throughout the experiments, whilst allowing the reaction products to exit the reactor in an aerosol form. At intervals, the latter was condensed in 10 mL test tubes cooled by iced water and capped with cotton wool. The samples were then analyzed by GC/MS.

Cleanup and shutdown of the reactor. Once the experiment was complete (typically after 2 h), the reactor was cooled to 80 °C. The flows of both CO_2 and 1-octene were stopped, while acetone was pumped at 1.5 mL min^{-1} to the catalytic bed. A second Shimadzu LC-10AS HPLC pump was used for this purpose (B in Scheme 2). After 20 min, acetone was switched with a scCO$_2$ flow at 1 mL min^{-1} for an additional 10 min. The reactor was finally cooled to room temperature while the pressure was slowly decreased to the ambient value.

The above described procedure was used to investigate the temperature, pressure, and flow rate effects. With all the other operations unchanged: (i) at 90 bar, the reaction step was carried out 35, 100, 110, 120 and 150 °C; (ii) at 100 °C, the BPR was set to 60, 90 and 150 bar during the experiments; (iii) at 100 °C and 90 bar, the flow rate of the 1-octene was set to 0.1 and 0.5 mL min^{-1}, respectively.

In the case of recycling experiments (Fig. 5 and 8), at 100 °C and 90 bar, the catalytic activation at 550 °C (part of step 1) and steps 2–3 of the above described procedure were repeated up to five times using the same catalytic bed.

General procedure for the CF-metathesis of 1-octene in the presence of liquid solvents

Steps 1 and 3 described for CF–scCO$_2$ reactions were also used for the CF-metathesis of 1-octene with liquid solvents (toluene and *n*-hexane, Fig. 8). The reaction step (2), however, was carried out through the following procedure: once the reactor was at 100 °C, the back pressure regulator (BPR) was set to the operating pressure of 90 bar. Using the valves V2 and V3, the N$_2$ flow used during the activation step (1) was stopped and the liquid solvent was pumped into the system through a Shimadzu LC-10AS HPLC pump (B in Scheme 2). After 5 min, 1-octene was also pumped through valve V1 in the same circuit of the solvent: a Shimadzu LC-10AS HPLC pump (A in Scheme 2) was used for this purpose. The flow rates of *n*-hexane and toluene were set to 2.98 and 2.45 mL min^{-1}, respectively, while the flow rate of 1-octene was set to 0.05 mL min^{-1}: this allowed us to operate with liquid solutions at the same molar fraction used for CF–scCO$_2$ experiments. These solutions went through a stainless-steel premixing chamber previously heated at 100 °C, and finally reached the reactor. At intervals, the reaction mixture was sampled from the reactor outlet and analyzed by GC/MS.

Characterization of 7-tetradecene, cross-metathesis and isomerization products

The structure of the main reaction product, 7-tetradecene (*cis* and *trans* isomers in 1 : 4 ratio), was assigned by its mass spectrum and by comparison to a commercial authentic sample. Other by-products derived from both the isomerization of the starting olefin (2-, 3-, and 4-octene) and cross-metathesis reactions (mainly, 2-nonene, 3-decene, 4-undecene, 5-dodecene, 6-tridecene), 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.[25] The full characterization data of all products were already reported by us in a previous paper.[7]

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11 The % amounts were determined by GC in two subsequent reactions: at the selected sampling times, these values did not differ by more than 7% from one experiment to another.

12 Data were taken from http://webbook.nist.gov

13 With respect to experiments of Fig. 1 and 2, the flow rate of 1-octene (F_{C_8}) was halved from 0.1 to 0.05 mL min^{-1}. Since the flow rate did not seem to affect the maximum reaction conversion (Fig. 3), a lower flow of the reactant would have plausibly allowed a longer lifetime to the catalyst.

14 The mole fraction of 1-octene [X_{C_8} = mol of 1-octene/(mol of 1-octene + mol of solvent)] appeared like a more appropriate parameter than the molar concentration, since X_{C_8} took into account the pressure of scCO$_2$ and the related solvation effects.

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