

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

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Abstract: The self-metathesis of α -olefins has been accomplished according to a procedure never previously reported, based on the combined use of heterogeneous catalysts (supported Re-oxides) and of supercritical carbon dioxide as the solvent. The reaction outcome is affected by the nature of the catalytic support (γ -Al₂O₃ and silica), and by the properties of compressed CO₂ which offers advantages in terms of replacement of conventional toxic solvents (e.g. *n*-heptane and toluene), of favourable reaction rates, and of easier recovery of final products.

Keywords: metathesis, Re-supported catalysts, supercritical CO₂.

1. Introduction

The metathesis of olefins is one of the best and more general carbon-carbon bond forming methodologies.¹ The reaction has also been acknowledged as the archetype Green Chemistry process, for clean productions of pharmaceuticals and polymer with reduced environmental emissions of hazardous wastes.² In this field however, notwithstanding the enormous efforts for the development of new catalysts able to extend the scope of the metathetic process,³ the replacement of conventional solvents, typically hexane, toluene, and dichloromethane,^{3,4} with alternative safer and *greener* media, have been poorly, if any, investigated. In particular, to the best of our knowledge, the combined use of heterogeneous catalysts and CO₂ solvent has never been claimed for the metathesis of olefins. We report here that in presence of Re₂O₇ supported on γ -Al₂O₃, not only the self-metathesis of α -olefins occurs efficiently in supercritical carbon dioxide (scCO₂), but interestingly, the reaction is more rapid than in *n*-heptane and toluene.

2. Experimental

The catalysts were prepared through conventional impregnation methods of aqueous solutions of NH₄ReO₄ over both γ -Al₂O₃ and silica, followed by calcination. The metathesis of 1-alkenes was performed in dense CO₂ at pressure of 80-150 bars. Since previous methodologies were not available, a new Schlenk apparatus was arranged *ad hoc*, to allow multiple operations under an inert (N₂) atmosphere: i) the activation of the catalyst at a high-temperature (550 °C); ii) the charge of the catalyst and of the reactant olefins (RCH=CH₂, R = C₄-C₆) in a stainless-steel autoclave; iii) the reaction step under CO₂ pressure. The method was also compared to conventional procedures carried out at atmospheric pressure, under liquid-phase conditions, using both *n*-heptane and toluene as solvents.

3. Results and discussion

Table 1 reports the results for the metathesis of 1-octene carried out at 35 °C, in presence of Re₂O₇ supported on both γ -Al₂O₃ and silica, and with different solvents. In all cases, regardless of the conditions

used, the formation of the product of self-metathesis (7-tetradecene, **1a**) is accompanied by different co-products identified as isomers of 1-octene (iso: 2-, 3-, and 4-octene) and linear olefins C₉-C₁₃. Data indicate that:

- i) Only the catalyst prepared on γ -Al₂O₃ is active for the transformation (entries 1-2, and 4). The different surface acidity between alumina and silica mostly account for this result.⁵
- ii) In scCO₂, the average reaction conversion is over 30% higher than in *n*-heptane and toluene. Plausible reasons are based on the gas-like diffusivity and viscosity and the liquid-like density of scCO₂, which may improve the mass transfer (with respect to conventional liquids).⁶
- iii) In all cases, the self-metathesis selectivity was of 95-98%.

Table 1. The metathesis of 1-octene over supported Re-oxides in different solvents

Entry	Cat. ^a	Solvent	Conv.'n (%,GC) ^b	t (h)	Products (% GC)			Selectivity (%) ^f
					iso ^c	C ₉ -C ₁₃ ^d	1a ^e	
1	Re-A	<i>n</i> -Heptane	38	2	1	1	36	95
2	Re-A	Toluene	42	2	1	1	40	95
3	Re-S	<i>n</i> -Heptane	1	2	1			
4	Re-A	scCO ₂ ^g	74	2	1	2	71	96
5	Re-S	scCO ₂ ^g	< 1	2	< 1			

^a Re-A: Re₂O₇ supported on γ -Al₂O₃; Re-S: Re₂O₇ supported on silica. ^b The reaction conversion (% by GC) was referred to all metathesis (olefins C₉-C₁₄) and isomerization compounds. ^c Amount of isomerization by-products (2-, 3- and 4-octene). ^d Amount of products of cross-metathesis (olefins C₉-C₁₃). ^e Amount of 7-tetradecene. ^f Selectivity towards 7-tetradecene. ^g scCO₂: 35 °C, 90 bar.

Similar results are obtained also in the metathesis of 1-hexene and 1-heptene carried out in presence of scCO₂ (Table 2).

Table 2. The self-metathesis of 1-hexene and 1-heptene carried out in scCO₂ (35 °C, 90 bar)

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

Footnotes a-c: see Table 1.

4. Conclusions

Overall, the combined use of heterogeneous and scCO₂ appears a viable alternative for the replacement of conventional liquid-phase methods ordinarily used in the metathesis of olefins.

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