The metathesis of α-olefins over supported Re-catalysts in supercritical CO_2

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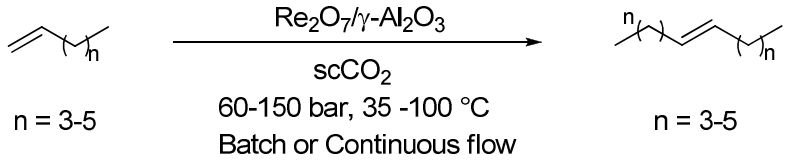
The metathesis of alkenes represents a paramount archetype of green synthesis with reduced emissions of hazardous wastes to the environment.[1] Nonetheless, the replacement of conventional media for the metathesis reaction - typically hydrocarbons or light chlorinated compounds – with safer and greener solvents, is a largely unexplored area. We report here that in the presence of heterogeneous catalysts such as Re_2O_7 supported on γ-Al_2O_3, not only the self-metathesis of α-olefins occurs efficiently in supercritical carbon dioxide ($scCO_2$) (Scheme), but it also takes place faster than in classic media (*n*-heptane, toluene and *n*-hexane).



The reaction has been investigated under both batch and continuous-flow conditions. Batch experiments showed that at 35 °C, in the presence of Re-oxide/γ-Al_2O_3, the self-metathesis of 1-olefins ($RCH=CH_2$, R=C4-C6) proceeded with a conversion over 30% higher on average, in $scCO_2$ (90 bar) than in a conventional solvent such as *n*-heptane. For instance, after 2 h, the average conversion of 1-octene was 67%, 40% and 36% in $scCO_2$, *n*-heptane and toluene, respectively. The product of self-methatesis, 7-tetradecene, was isolated in yields up to 68%.[2]

Continuous-flow (c.-f.) experiments were carried out in a plug-flow reactor filled with a catalytic bed of Re-oxide supported on γ-Al_2O_3. $scCO_2$ and *n*-hexane were used as solvents for the self-metathesis of 1-octene. Compared to the hydrocarbon medium, the supercritical phase allowed residence times up to five-fold lower to reach similar reaction conversions (40-50%). Alike to batch conditions, c.-f. experiments proved that $scCO_2$ as a solvent could improve both productivity and yield for the alkene metathesis.

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[1] W. F. Carroll, Jr. http://pubs.acs.org/pressrelease/nobelprize/2005.html

[2] M. Selva, A. Perosa, M. Fabris and P. Canton, *Green Chem.* 2009, **11**, 229-238