The metathesis of $\alpha$-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$_2$O$_7$ supported on $\gamma$-Al$_2$O$_3$, not only the self-metathesis of $\alpha$-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/$\gamma$-Al$_2$O$_3$, 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-metathesis, 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 $\gamma$-Al$_2$O$_3$. 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.


$^2$ M. Selva, A. Perosa, M. Fabris and P. Canton, Green Chem. 2009, 11, 229-238