

Metathesis of unsaturated fatty acid methyl esters with tungsten and rhenium-based catalysts – a comparison

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Abstract: Olefin metathesis is an industrially important process suitable for controlling the chain length of the fatty acid components of natural oils. Self-metathesis of fatty acid esters results in a mixture of *n*-olefins, monoesters and diesters. The latter are platform compounds for the synthesis of high-value products in the fragrance, polymer and fine chemicals industries. In this report the metathesis activity and selectivity of tetraalkyl tin-promoted homogeneous $W(O-2,6-C_6H_3X_2)_2Cl_4$ and the heterogeneous 3 wt% $Re_2O_7/SiO_2-Al_2O_3$ catalytic systems on unsaturated C18 FAMES is compared and the possible deactivation pathways are discussed. [The Journal of American Science. 2009;5(1):40-44]. (ISSN: 1545-1003).

Keywords: metathesis, FAMES, $W(O-2,6-C_6H_3X_2)_2Cl_4$, $Re_2O_7/SiO_2-Al_2O_3$

Introduction

Olefin metathesis is an industrially important reaction capable of controlling the chain length of fatty acid components of natural oils. In the presence of a metal-carbene complex, groups around the carbon-carbon double bonds rearrange to form new olefinic compounds.¹ New metathesis products could range anything from short- to long-chain olefins and from mono- to difunctionalised olefins. Warwel *et al.*^{2,3} for example, reported the conversion of olefinic fatty acid methyl esters to ω -olefinic esters *via* ethenolysis using the heterogeneous rhenium and the homogeneous ruthenium catalysts. ω -Olefinic esters were subsequently converted to polyolefins, polyesters and polyethers. Dicarboxylic esters obtained by metathetical dimerization of ω -olefinic methyl esters were converted to polyesters by polycondensation with petrochemical diols. Tsuji and Hashiguchi⁴ reported the conversion of oleic acid ethyl ester to diethyl 9-octadecene-1,18-dioate (diester) *via* a metathesis reaction and subsequently cyclized the product by Dieckmann cyclization reaction. The cyclized product was decarboxylated to give civetone as a mixture of *cis* and *trans* isomers. The latter is an important ingredient of musk perfumes.

We consider, herein, the self-metathesis of unsaturated C18 FAMES in the presence of the homogeneous $W(O-2,6-C_6H_3X_2)_2Cl_4/SnMe_4$ ($X = Cl, Ph$) and the heterogeneous 3 wt% $Re_2O_7/SiO_2-Al_2O_3/SnBu_4$ catalytic systems. Promoted with a tetraalkyltin compound, these catalysts are active and selective under mild reaction conditions. The activity and selectivity of $W(O-2,6-C_6H_3X_2)_2Cl_4/SnMe_4$ catalytic system could be changed by changing the X-substituent on the aryloxide ligand. In this paper a comparison of the catalytic activities and selectivities of $W(O-2,6-C_6H_3X_2)_2Cl_4$ and Re_2O_7 catalytic systems is made and the possible deactivation pathways are discussed.

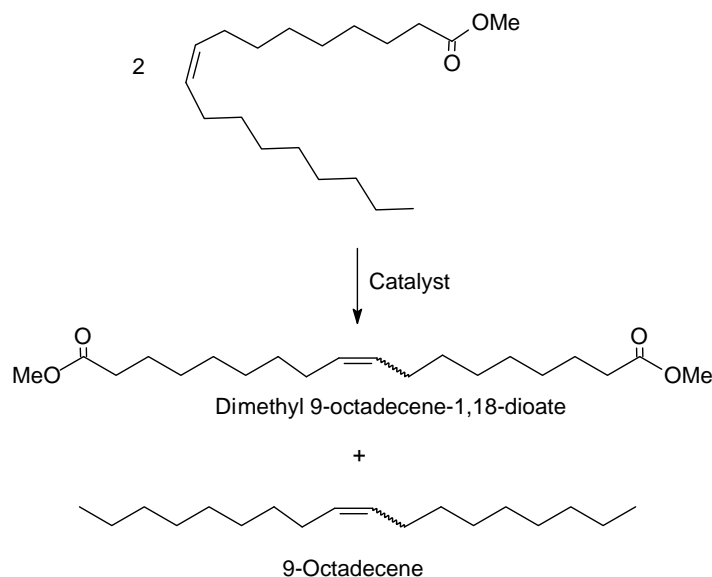
Materials and Methods

Reagents were purchased from Aldrich and silica alumina from Akzo. Chlorobenzene (solvent) was dried by refluxing over P_2O_5 , distilled and stored under N_2 . Substrates were purified by passing through activated silica alumina and all reaction manipulations were performed using standard Schlenk tube techniques under N_2 atmosphere. Reactions were carried out as described previously^{5,6} and the reaction progress was followed by a gas chromatograph equipped with a flame ionisation detector (FID) and a DB-1 capillary column. Characterisation of products was carried out using gas chromatography-mass spectrometry (GC/MS).

Results and Discussion

Activity and selectivity of W and Re-based catalysts

Methyl esters of oleic and linoleic acids were converted by a metathesis reaction using $W(O-2,6-C_6H_3X_2)_2Cl_4/SnMe_4$ and 3 wt% $Re_2O_7/SiO_2-Al_2O_3/SnBu_4$ catalytic systems. Metathesis of methyl oleate gives two primary products, namely, 9-octadecene and dimethyl 9-octadecenedioate as shown in Scheme 1. Using methyl oleate:Re molar ratio of 60, the substrate conversion of 50% (at 20°C) was obtained after 2 h reaction time yielding equimolar amounts of 9-octadecene and dimethyl-9-octadecenedioate. The oleate conversion compared favourably with the results obtained by Sibeijn and Mol⁷. Selectivity towards primary metathesis products was 99%, indicating that side reactions, for example, double bond isomerization, were less prominent under the prevailing reaction conditions. This observation is in agreement with the previous findings by Mol and Andreini.⁸ On the other hand, a methyl oleate conversion of 50% and 48% was obtained in the presence of $W(O-2,6-C_6H_3Ph_2)_2Cl_4/SnMe_4$ and $W(O-2,6-C_6H_3Cl_2)_2Cl_4/SnMe_4$ catalytic systems, respectively, with oleate:W molar ratio of 60 at 85 °C. $W(O-2,6-C_6H_3Ph_2)_2Cl_4/SnMe_4$ was, therefore, more active than $W(O-2,6-C_6H_3Cl_2)_2Cl_4/SnMe_4$ which is a clear indication that electronic effects were more prominent than steric properties in this particular case. Dimethyl 9-octadecenedioate can be converted to civetone *via* Diekmann condensation and is also an attractive feedstock for the synthesis of polyesters and polyamides.⁹ Dimerization of 9-octadecene results in a lube oil range hydrocarbon intermediate.⁹



Scheme 1. Metathesis of methyl oleate

Upon the metathesis of methyl linoleate, a mixture consisting of *n*-olefins, olefinic monocarboxylic and dicarboxylic esters was obtained. Using a 3 wt% $Re_2O_7/SiO_2-Al_2O_3/SnBu_4$ with substrate:Re molar ratio of 60 a conversion of 85% and a selectivity of 99% was obtained in 2 h reaction time at 20 °C. The yields obtained for *n*-olefins, monocarboxylic esters and dicarboxylic esters were 28, 51.5 and 20.5%, in that order. However, at elevated reaction temperatures (> 80 °C), the Re_2O_7 system gave relatively lower substrate conversions. On the other hand the $W(O-2,6-C_6H_3X_2)_2Cl_4/SnMe_4$ catalytic systems (X = Ph, Cl) required slightly elevated temperatures (85 °C) to reach optimal activity. Table 1 shows the activities and selectivities of Re_2O_7 and $W(O-2,6-C_6H_3X_2)_2Cl_4$ catalytic systems for comparison.

Table 1. Activity and selectivity of $W(OAr)_2Cl_4/SnMe_4$ and $Re_2O_7/SiO_2-Al_2O_3/SnBu_4$ catalytic systems (ester: M^{n+} molar ratio = 60, solvent = PhCl, $OAr = O-2,6-C_6H_3X_2$)					
	Sn/Re	Temp/ $^{\circ}C$	Time	Conv/%	Selectivity/%
Re_2O_7					
Methyl oleate	0.6	20	2	50	99
Methyl linoleate	0.6	20	2	85	99
Methyl linoleate	0.6	60	2	87	99
$W(OArPh_2)_2Cl_4$					
Methyl oleate	3	85	2	50	98
Methyl linoleate	3	85	2	95	98
$W(OArCl_2)_2Cl_4$					
Methyl oleate	3	85	2	48	98
Methyl linoleate	3	85	2	78	98

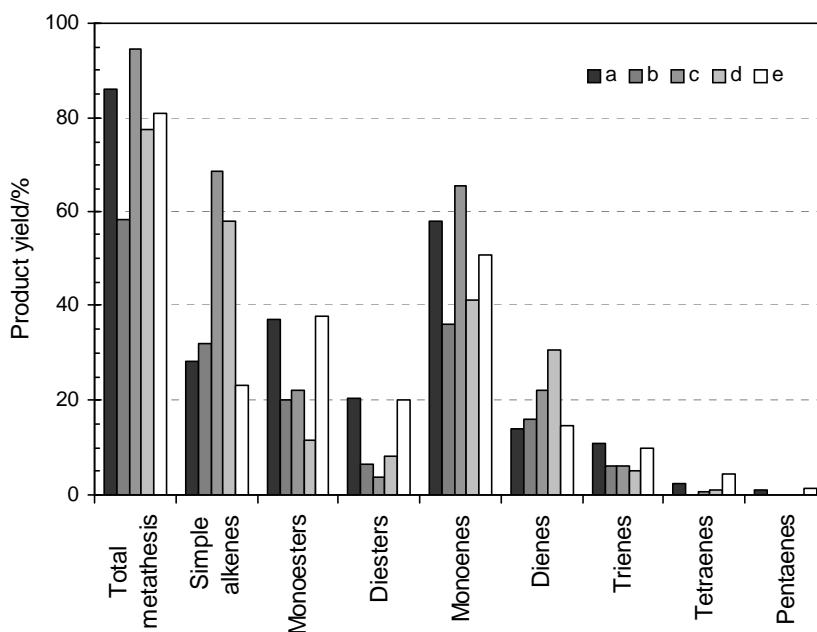


Figure 1 Yields obtained (mol%) upon metathesis of methyl linoleate with Re and W-catalysts. **a.** Powder 3% $Re_2O_7/SiO_2 \cdot Al_2O_3$, **b.** Extrudate 3 wt% $Re_2O_7/SiO_2 \cdot Al_2O_3$, **c.** $W(OArPh_2)_2Cl_4/SnMe_4$, **d.** $W(OArCl_2)_2Cl_4/SnMe_4$, **e.** $WCl_6/SnMe_4$

The homogeneous $W(O-2,6-C_6H_3Ph_2)_2Cl_4/SnMe_4$ was the most active catalytic system with methyl linoleate conversion of 95% compared to Re_2O_7 (87% at 60 $^{\circ}C$) and $W(O-2,6-C_6H_3Cl_2)_2Cl_4/SnMe_4$ (78%). Both Re and W catalysts were highly selective (98%) towards primary metathesis products. However, the $W(O-2,6-C_6H_3X_2)_2Cl_4/SnMe_4$ catalytic systems were less selective towards diesters as compared to a 3wt% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$ catalyst. Figure 1 compares the yields obtained in the metathesis of the methyl linoleate. The results obtained from the literature¹⁰ using $WCl_6/SnMe_4$ catalyst are

included for comparison. Despite the high catalytic activity of $W(O-2,6-C_6H_3Ph_2)_2Cl_4/SnMe_4$, the latter was less selective towards diesters (4 mol%) compared to $W(O-2,6-C_6H_3Cl_2)_2Cl_4/SnMe_4$ (10.8 mol%), 3wt% $Re_2O_7/SiO_2 \cdot Al_2O_3/SnBu_4$ (20.5 mol%) and the classical $WCl_6/SnMe_4$ (28 mol%).

Catalyst Deactivation

As mentioned earlier, catalyst deactivation is one of the primary obstacles hindering commercialisation of the metathesis of functionalised olefins. In most cases reaction equilibrium is reached within 2–4 h reaction time after which the catalyst goes essentially “dead”. Possible causes for deactivation of the Re-catalyst include among others, the presence of impurities (oxygenates) in the substrate, site covering and pore-mouth plugging resulting from coke formation and adsorption of polymeric products thus blocking the catalytic active sites, reductive elimination of the metallacyclobutane intermediate and a Wittig-type reaction between the substrate ester group and the rhenium carbene. As the main cause of deactivation Spronk and Mol¹¹ proposed an intrinsic mechanism in which the metallacyclobutane is reductively eliminated in two possible routes, namely, the formation of cyclopropane or β -elimination to form an alkene. Although the turnover numbers are relatively low for the Re_2O_7 -catalyst, this is compensated for by the fact that the Re_2O_7 catalyst can be regenerated several times by calcination at 500–550 °C and the addition of the promoter.^{9,11}

For tungsten-based catalysts, the previous studies^{6,12,13} have shown that $W(O-2,6-C_6H_3Ph)_2Cl_4/SnMe_4$ is generally more resistant to deactivation than its chlorinated ($X=Cl$) counterpart in the presence of air and oxygenates. The relatively easy deactivation of $W(O-2,6-C_6H_3Cl_2)_2Cl_4/SnMe_4$ catalyst could be attributed to the high electrophilic nature of the W atom arising from the highly electron-withdrawing Cl atoms on the *o,o'*-positions of the aryloxy ligand. This renders the W atom more susceptible to attack by electron-rich oxygenates, for example, the ester group in this case. However, the phenyl substituent ($X=Ph$) on the aryloxy ligand is less electron-withdrawing and thus susceptibility to attack by oxygenates is relatively less.

Summary and Concluding Remarks

The heterogeneous 3wt% $Re_2O_7/SiO_2 \cdot Al_2O_3$ and the homogeneous $W(O-2,6-C_6H_3X_2)_2Cl_4$ catalysts, both promoted with a tetraalkyltin compound, are amongst the promising catalytic systems for the metathesis of functionalised olefins. These catalysts require relatively mild reaction conditions and have a high selectivity towards primary metathesis products. The ability to alter electronic and steric properties of the aryloxy ligands in $W(O-2,6-C_6H_3X_2)_2Cl_4$ catalysts makes it possible to control the activity and sometimes even the stereoselectivity of these catalysts. Replacing X with a less electron withdrawing group such as phenyl group renders the $W(O-2,6-C_6H_3X_2)_2Cl_4$ catalyst more resistant to deactivation than when X is a highly electron-withdrawing group, for example, the Cl group. Results have also shown that the substituent X has a significant influence on product selectivity, thus suggesting a more considered approach for one to achieve the expected outcomes. On the other hand the supported Re_2O_7 catalyst has an advantage in that it is already active at ambient temperature, can be regenerated over a number of times and is easily separated from the product stream.

Acknowledgement

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