



# Valorisation of vegetable oils by heterogeneous catalysis via metathesis reactions

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The metathesis of unsaturated fatty acid methyl esters (FAME) to obtain value-added chemicals is becoming increasingly attractive in oleochemistry. Nevertheless, there is a need to develop efficient solid catalysts for FAME metathesis that would allow straightforward catalyst separation and recovery. In this work, the main advances achieved lately using novel heterogeneous catalysts for the homo-metathesis of methyl oleate and the cross-metathesis of methyl oleate with lower olefins are analyzed.

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## Introduction

Nowadays, basic oleochemicals such as unsaturated fatty acid methyl esters (FAME) may be obtained by simple industrial processes from vegetable oils and are then cheap and readily available feedstocks for the synthesis of valuable chemicals. Most of oleochemical reactions of FAME are carried out in the carboxy functions, but the synthesis of useful polymer intermediates and fine chemicals via reactions of the C=C bond such as metathesis reactions is becoming increasingly attractive at industrial level [1]. Homogeneous catalysts have been widely employed for promoting the metathesis of triacylglycerols and unsaturated fatty acid derivatives, although their performance may be often limited by their tolerance towards the carboxylic acid or ester groups. In particular, FAME metathesis has been studied using mainly Grubbs' Ru alkylidenes and second-generation Ru Hoveyda-Grubbs (HG2) complexes that show great tolerance towards functional groups, moisture and oxygen. However, the industrial application of homogeneous olefin metathesis catalysts is hampered by the difficulties associated with removing ruthenium from

the reaction media and the expensive separation/recovery steps required to obtain high-purity products. Thus, the development of an efficient process using solid catalysts is a highly desirable technological target for the metathesis of oil-derived functionalized olefins. Nevertheless, classical solid olefin metathesis catalysts ( $\text{WO}_3$ ,  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ ) have been of limited applicability for the synthesis of fine chemicals by FAME metathesis because they required either severe reaction conditions or coactivators to reach high catalytic activity. Immobilization of homogeneous catalysts on high surface area porous supports may combine advantages of homogeneous and heterogeneous catalysts and allows the Ru recovery. The immobilization procedure should be achieved without modification of the catalyst to keep the optimized ligand systems of the homogeneous catalysts. The classical strategies to anchor Ru-like complexes to the surface by covalent linkages via different types of ligands have been recently detailed in several reviews [2,3]. Unfortunately, these immobilization methods require a rather complicated and laborious synthesis involving several steps and additional reagents that make them less accessible to reactants and limit their practical application. Alternative non-covalent immobilization strategies involving either weak physical interactions between the Ru complex and the surface or one-step mechanochemical immobilizations were then developed to avoid complicated modifications of either catalyst partner [4,5]. Ruthenium leaching may be significant if heterogeneous catalysts prepared by soft adsorption (physisorption) of the Ru complex on the support are used in polar solvents, in particular for the metathesis of functionalized olefins such as FAME.

Several reports were published in the last five years on the metathesis of FAME using novel heterogeneous catalysts consisting either of supported methyltrioxorhenium ( $\text{CH}_3\text{ReO}_3$ , MTO) or Grubbs' Ru alkylidene complexes immobilized by physisorption on different supports ( $\text{SiO}_2$ , MCM-41, SAB-15). In this work, we present the main results obtained for two types of FAME metathesis reactions, using methyl oleate (MO) as a model molecule: i) the self-metathesis of methyl oleate, and ii) the cross-metathesis of methyl oleate with lower olefins.

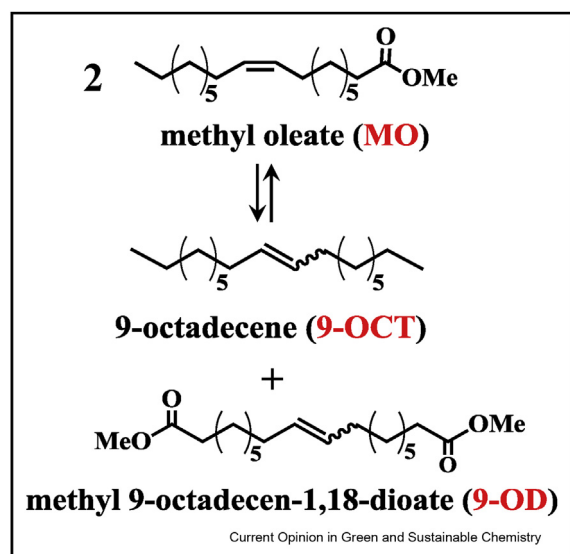
## Self-metathesis of methyl oleate

The self-metathesis of methyl oleate, a model molecule of bulky triglycerides present in vegetable oils, yields 9-octadecene-1,18-dioate (9-OD) and 9-octadecene (9-

OCT), as depicted in Figure 1. Unsaturated diesters such as 9-OD are widely used for producing polymers and fine chemicals and their catalytic synthesis via the self- and cross-metathesis of FAME was one of the first reactions investigated in oleochemistry. The MO self-metathesis was studied in the 90's using  $\text{Re}_2\text{O}_7/\text{SiO}_2\text{-Al}_2\text{O}_3$  promoted with  $\text{SnBu}_4$  and methyltrioxorhenium supported on alumina. Recently, Belkacemi et al. [6–8] reported that MTO supported on  $\text{ZnCl}_2$ -modified mesoporous alumina efficiently catalyze the self-metathesis of methyl oleate. They impregnated 3 wt.% MTO on  $\text{ZnCl}_2\text{-Al}_2\text{O}_3$  of Al/Zn = 8 M ratio and observed that its activity for MO self-metathesis was significantly higher as compared to a 3 wt.% MTO/ $\text{Al}_2\text{O}_3$  catalyst. In terms of turnover numbers (TON, mol of metathesis products/mol of catalyst), TON values of 3314 and 420 were determined on 3 wt.% MTO/ $\text{ZnCl}_2\text{-Al}_2\text{O}_3$  and 3 wt.% MTO/ $\text{Al}_2\text{O}_3$ , respectively, under similar reaction conditions. The superior activity of 3 wt.% MTO/ $\text{ZnCl}_2\text{-Al}_2\text{O}_3$  catalyst was explained by considering that terminal OH groups of mesoporous alumina react with  $\text{ZnCl}_2$  and generate proper surface site structures for MTO grafting, thus enhancing the catalyst activity towards MO metathesis in comparison to those generated by MTO grafting on non-modified mesoporous alumina. Zelin et al. [9] studied the self-metathesis of MO on second generation Ru Hoveyda-Grubbs complex supported on silica ( $\text{HG2}/\text{SiO}_2$ ). HG2 was immobilized by impregnating the silica with a solution of HG2 in cyclohexane at 298 K. The reaction was conducted in cyclohexane at 303–323 K using HG2 loadings between 0.43 and 1.67 wt.%. The MO equilibrium conversion and the 9-OD and 9-OCT equilibrium yields were rapidly reached on  $\text{HG2}/\text{SiO}_2$  catalysts,

being the carbon balance near 100%. No HG2 leaching from the catalyst was detected in cyclohexane reflecting effective HG2 immobilization on the silica surface. The initial MO conversion turnover rate ( $\text{TOF}^0$ , mol MO/mol HG2 min) was almost the same on  $\text{HG2}/\text{SiO}_2$  catalysts containing up to 1.67% HG2, thereby showing that the intrinsic activity of HG2 complex does not change with the HG2 loading. Nevertheless, the TOF for MO self-metathesis on  $\text{HG2}/\text{SiO}_2$  was about three times lower as compared to that obtained using dissolved HG2 via homogeneous catalysis. Balcar et al. [10] investigated the self-metathesis of MO on Ru Hoveyda-Grubbs type catalysts with cationic tags on NHC ligands ( $\text{HG2N}^+\text{Cl}^-$ ) immobilized on mesoporous silica SBA-15 and zeolites MCM-22, MCM-56 and MCM-36. Catalysts were prepared according to [11] and the reaction was carried out in toluene at 313 K.  $\text{HG2N}^+\text{Cl}^-/\text{SBA-15}$  was more active than samples containing the  $\text{HG2N}^+\text{Cl}^-$  complex immobilized on zeolites. In all cases, 9-OCT and 9-OD were the only reaction products. Authors attributed the lower activity of  $\text{HG2N}^+\text{Cl}^-/\text{zeolite}$  samples to restrictions in methyl oleate coordination because of some confinement in the coordination sphere of Ru due to complex immobilization. Cabrera et al. [12] compared the catalytic performance for MO self-metathesis of a  $\text{HG2}/\text{SiO}_2$  catalyst prepared by physisorption with an analogous complex with an H2ITap ligand (1,3-bis(2',6'-dimethyl-4'-dimethyl aminophenyl)-4,5-dihydroimidazol-2-ylidene) supported on silica. Both catalysts were tested in a continuous-flow reactor at 433 K and 2 bar by feeding MO in cyclohexane (50 wt.%) at 2 mL/min. The silica-supported H2ITap-modified HG2 catalyst was more active (TON = 4950) and stable than  $\text{HG2}/\text{SiO}_2$  (TON = 3350) but showed a significant Ru leaching and loosed 19% Ru after 8 h on stream.

Figure 1

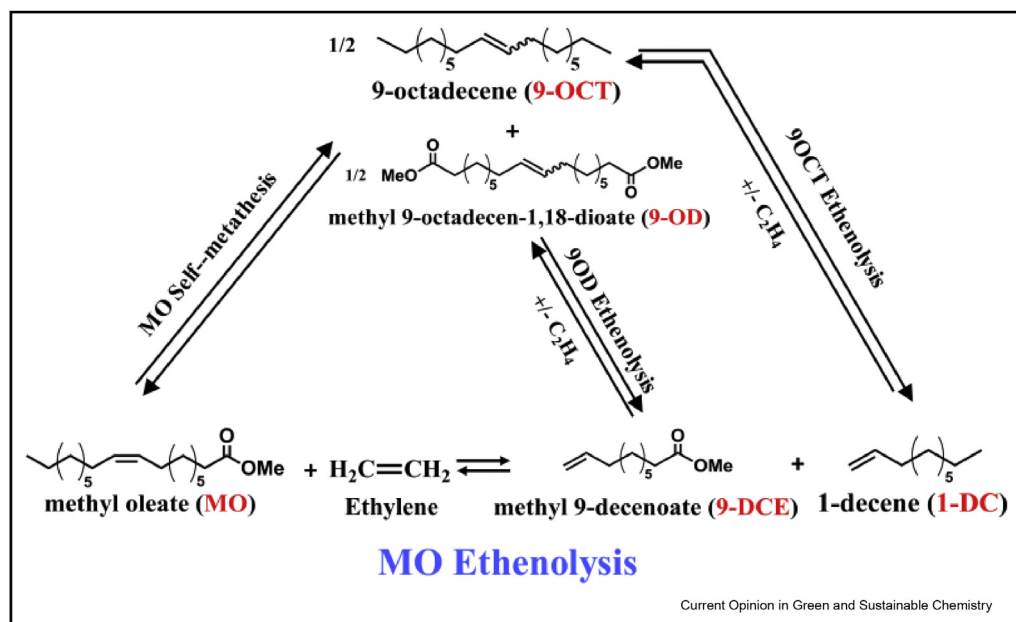


Self-metathesis of methyl oleate.

### Cross-metathesis of methyl oleate with lower olefins

The cross-metathesis of FAME with lower olefins such as ethylene, 2-butene and 1-hexene has been investigated to afford less abundant medium-chain fatty acid esters with extensive use in cosmetics, detergents and polymer additives. In particular, the development of efficient catalysts for the cross metathesis of MO with ethylene (ethenolysis) is a critical target for the conversion of vegetable oil based feedstocks into valuable raw materials for many applications in polymers, fragrances and surfactants. As shown in Figure 2, the reaction yields methyl 9-decenoate (9-DCE) and 1-decene (1-DC). 9-DCE is used in perfumery and for the synthesis of pheromones, prostaglandins and polymers, while 1DC is a monomer of useful copolymers, surfactants and lubricants. The reaction network of MO ethenolysis includes the self-metathesis of MO that produces 9-OCT and 9-OD, which may in turn react with ethylene to form 9-DCE and 1-DC (Figure 2). The

Figure 2



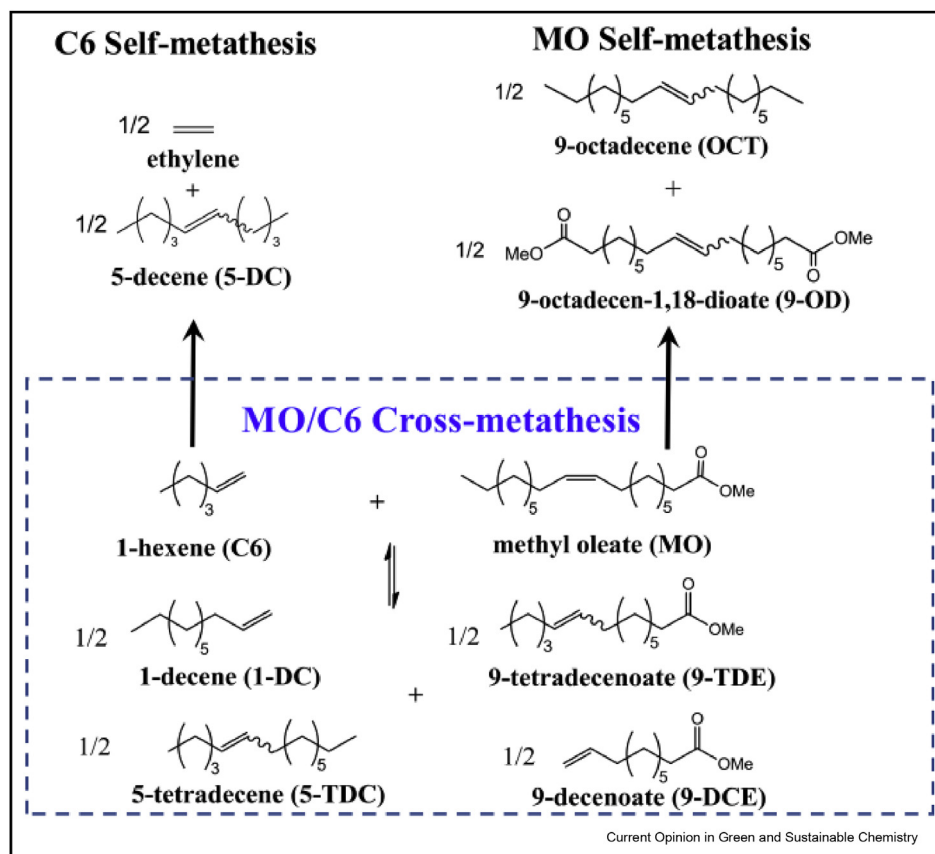
Reaction network for the cross-metathesis of methyl oleate with ethylene.

ethenolysis of MO has been essentially investigated with homogeneous catalytic systems based on well-defined metal carbene complexes. A recent review presents the main results obtained using metal carbene complexes of ruthenium, molybdenum and tungsten [13]. In heterogeneous catalysis, the ethenolysis of MO was studied in the 90's on  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  and  $\text{CH}_3\text{ReO}_3$  supported on  $\text{SiO}_2\text{-Al}_2\text{O}_3$ . Recently, Nieres et al. investigated this reaction on  $\text{HG}_2(10\%)/\text{SiO}_2$  catalysts, using a batch slurry reactor at 313–353 K and 2.5–7.5 bar of  $\text{C}_2\text{H}_4(5\%)/\text{N}_2$  [14]. Kinetic studies showed that the reaction mechanism for the formation of MO ethenolysis products, 9-DCE and 1-DC, on  $\text{HG}_2(10\%)/\text{SiO}_2$  involves the rapid MO conversion to 9-OD and 9-OCT via MO homo-metathesis, followed by the cross-metathesis of MO, 9-OD and 9-OCT with ethylene (Figure 2). The yield and selectivity to ethenolysis products increased with ethylene pressure, essentially because the increase of the  $\text{C}_2\text{H}_4/\text{MO}$  ratio shifts the equilibrium to high MO conversions and suppresses the MO self-metathesis competitive reaction. Nevertheless, deactivation of  $\text{HG}_2/\text{SiO}_2$  catalysts also increased with ethylene pressure probably because of the low stability of methylidene intermediates leading to hydride species that may suppress the metathesis cycle. The highest values of ethenolysis product yield (63%) and selectivity (77%) were obtained at 313 K and  $P_{\text{C}_2\text{H}_4} = 0.250$  bar. Under these reactions conditions, the turnover frequency for the initial formation rate of ethenolysis products was  $\text{TOF}_E^0 = 52.7 \text{ h}^{-1}$ . Authors confirmed

that no Ru leaching takes place using cyclohexane as solvent.

The cross-metathesis of MO with 1-hexene (C6) was studied recently on  $\text{HG}_2/\text{SiO}_2$  catalysts containing between 0.87 wt.% and 11.6 wt.%  $\text{HG}_2$  by Zelin et al. [15]. The reaction produces 1-DC, 9-DCE, methyl 9-tetradecenoate (9-TDE) and 5-tetradecene (5-TDC) as depicted in Figure 3; secondary reactions are the self-metathesis of MO and self-metathesis of 1-hexene. 9-TDE is used for the synthesis of biodegradable pheromones employed for the control of insect pests. The main results obtained on  $\text{HG}_2(3.36\%)/\text{SiO}_2$  by increasing the 1-hexene/methyl oleate molar ratio ( $R_{\text{C}_6/\text{MO}}$ ) are shown in Table 1. When  $R_{\text{C}_6/\text{MO}}$  was increased from 1 to 7, the MO conversion increased from 67% to 93% and the yield to cross-metathesis products ( $Y_{\text{C-M}}$ ) from 46% to 87%. Consistently, the selectivity to cross-metathesis products ( $S_{\text{C-M}}$ ) increased from 59 to 93% at the expense of  $S_{\text{S-MO}}$ , the selectivity to MO self-metathesis products, by varying  $R_{\text{C}_6/\text{MO}}$  from 1 to 7. Furthermore, the increase of  $R_{\text{C}_6/\text{MO}}$  ratio promoted the preferential formation of terminal olefins (1-DC, 9-DCE) among the MO/C6 cross-metathesis products, which was attributed to the concomitant increase of the concentration of C6 self-metathesis products, in particular ethylene. In summary, the work of Zelin et al. [16] shows that high yields (87%) and selectivities (93%) to MO/1-hexene cross-metathesis products are obtained on  $\text{HG}_2/\text{SiO}_2$

Figure 3



Cross-metathesis of methyl oleate with 1-hexene.

Table 1

Catalytic results for the cross-metathesis of methyl oleate with 1-hexene. From Ref. [15].

Reactant ratio	Initial 1-hexene concentration	Conversion <sup>a</sup>		Yield <sup>a</sup>		Selectivity <sup>a</sup>		Carbon balance		
		$R_{C_6/MO}$	$C_{C_6}^0$ (mol/L)	$X_{MO}$ (%)	$X_{C_6}$ (%)	$Y_{C-M}$ (%)	$Y_{S-MO}$ (%)	$S_{C-M}$ (%)	$S_{S-MO}$ (%)	CB (% C)
1	0.029			67	66	46	21	59	41	94
2	0.058			75	61	55	20	73	27	96
3	0.087			84	56	69	15	82	18	95
4	0.016			88	50	78	10	89	11	97
5	0.145			91	40	83	8	91	9	95
6	0.174			92	34	86	6	93	7	95
7	0.203			93	28	87	6	93	7	99

Catalyst: HG2(3.36%)/SiO<sub>2</sub>, T = 303 K;  $C_{MO}^0 = 0.029$  M,  $W_{cat} = 100$  mg, cyclohexane (10 ml).

<sup>a</sup> At the end of catalytic runs.

catalysts when using high 1-hexene concentrations to suppress secondary self-metathesis reactions.

## Conclusions

Novel hybrid solid catalysts consisting of either methytrioxorhenium complex supported on suitable acid

supports or immobilized Grubbs-type alkylidene complexes efficiently promote FAME metathesis reactions such as the homo-metathesis of methyl oleate and the cross-metathesis of methyl oleate with lower olefins. Nevertheless, more studies are needed for developing stable and regenerable heterogeneous metathesis catalysts for converting FAME to valuable chemicals.

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