Valorization of Vegetable Oils via Metathesis Reactions: Cross-Metathesis of Methyl Oleate with 1-Hexene on Supported Hoveyda-Grubbs catalysts

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Introduction

Fatty acid methyl esters (FAME) are usually obtained from the transesterification of natural oils and fats with lower alcohols. Most of all oleochemistry reactions of FAME are carried out in the carboxy functions, but the synthesis of products formed by reactions of the C=C bonds such as epoxidation, metathesis and ozonolysis is becoming increasingly important at industrial level. FAME metathesis has been studied in homogeneous catalysis using mainly Grubbs' Ru complexes. In particular, second generation Hoveyda-Grubbs (H-G) Ru catalysts present high activity and selectivity, and exhibit remarkable stability to the presence of moisture and oxygen. Nevertheless, only a limited number of industrial processes use homogeneous olefin metathesis because of the high cost of Ru complexes, the difficulties associated with removing ruthenium from the reaction media and the expensive separation/recovery steps required to obtain high-purity products. This situation turns clearly attractive the development of active and stable immobilized supported complexes that would allow straightforward catalyst separation. However, very few papers deal with the use of supported H-G catalysts for the metathesis of functionalized substrates [1]. Cross-metathesis of FAME with lower olefins allows shortening of the long-chain FAME molecules to form less abundant medium-chain fatty acid esters that are valuable intermediates in fine chemistry. Here, we study the cross-metathesis of methyl oleate (MO) with 1-hexene (C6) on silica-supported Hoveyda-Grubbs complexes (Figure 1). 9-TDO is a valuable pheromone precursor while 9-DCO is used in the synthesis of fragrances and prostaglandins.

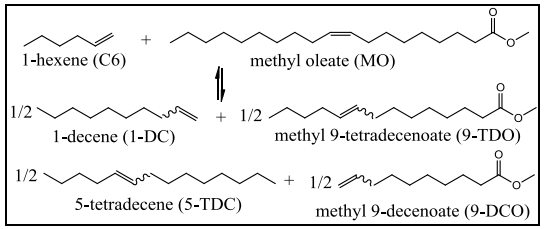

Figure 1: Cross-metathesis of MO with C6

Materials and Methods

The HG(1.2%)/SiO_2 sample was prepared by impregnating a commercial silica with a solution of HG in cyclohexane. The cross-metathesis of MO with C6 was carried out in a glass batch reactor at 101.3 kPa, between 303 and 323K, using cyclohexane as solvent. Besides the cross-metathesis reaction products, it was observed the formation of 9-octadecene (9-OD) and 9-octadecen-1,18 dioate (9-OCT) from the self-metathesis of MO. No compounds derived from the self-metathesis of 1-hexene were detected.

Results and Discussion

Catalyst characterization by XRD, FTIR and DRIFT techniques showed that the HG complex was highly dispersed on the SiO_2 surface. On the other hand, it was verified that no HG lixiviation took place in cyclohexane during the progress of the reaction. Table 1 shows the results obtained at 303K using different C6/MO concentration ratios ($R_{C6/MO}$). In all the cases, the carbon balance (CB) was higher than 95%. The reaction was limited by equilibrium reaching the MO conversion a value of X_{MO}^{eq} = 93% at 303K for $R_{C6/MO}$ = 5. When the catalytic run was performed using $R_{C6/MO}$ = 1, the reaction rapidly attained the MO conversion equilibrium (64%) forming a mixture of cross-metathesis (selectivity S_{C-M}^{f} = 56%) and MO self-metathesis (S_{MO-S}^{f} = 44%) products. In an attempt to enhance the yield to cross-metathesis products, additional catalytic runs at higher C6 concentrations were carried out in order to suppress self-metathesis of MO. The initial MO conversion rate (r_{MO}^{0}) decreased with C_{C6}^{0} (Table 1), resulting a negative order in C6 of about -1. In contrast, S_{C-M}^{f} increased with C_{C6}^{0} reaching 89% for $R_{C6/MO}$ = 3 and 91% for $R_{C6/MO}$ = 5. For $R_{C6/MO}$ = 3, the MO conversion at the end of the run, X_{MO}^{f}, was 78%, thereby yielding about 70% of cross-metathesis products. Figure 2 shows the evolution of yields as a function of time for the catalytic run carried out at $R_{C6/MO}$ = 3. For $R_{C6/MO}$ = 5, X_{MO}^{f} was only 23% revealing the in-situ catalyst deactivation when high C6 concentrations are employed. Probably, terminal olefin C6 forms with H-G complex unstable propagating methylidene species leading to hydride species that suppress the metathesis cycle, as suggested in [2]. Increasing the C6 concentration improves therefore the selectivity to cross-metathesis products but accelerates the HG(1.2%)/SiO_2 activity decay.

Table 1: Catalytic results

C_{C6}^{0} (M)	$R_{C6/MO}$ (molar)	r_{MO}^{0} (mmol/g h)	X_{MO}^{eq} (%)	X_{MO}^{f} (%)	S_{C-M}^{f} (%)	S_{MO-S}^{f} (%)	CB (%)
0.029	1	12.8	64	64	56	44	96
0.087	3	4.0	85	78	89	11	99
0.0145	5	3.1	93	23	91	9	100

HG(1.2%)/SiO_2, 303 K, W_{cat} = 100 mg

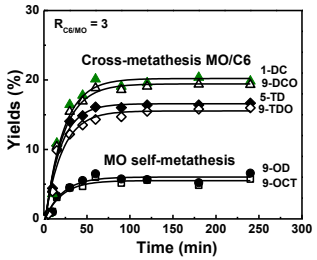

Figure 2: Cross-metathesis MO/C6

Significance

Yields to cross-metathesis products of about 70% are obtained at 303K from the reaction between methyl oleate and 1-hexene on SiO_2-supported Hoveyda-Grubbs complexes.

References

1. Zelin, J., Trasarti, A.F., Apesteguía, C.R. *Catal. Comm.* 42, 84 (2013).
2. Hong, H., Wenzel, A., Salguero, T., Day, M., Grubbs, R. *J. Am. Chem. Soc*. 129, 7961 (2007).