

PLANT OIL VALORIZATION BY CROSS-METATHESIS REACTIONS: SYNTHESIS OF FINE CHEMICALS FROM METHYL OLEATE

A.F. TRASARTI, E.J. GONZÁLEZ, P.D. NIERES and C.R. APESTEGUÍA

*Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, Predio CCT CONICET
Paraje El Pozo, 3000 Santa Fe, Argentina.
capesteg@fiq.unl.edu.ar*

Abstract— This work studies the production of high-value compounds by the cross-metathesis of methyl oleate (MO) with ethylene, cinnamitrile and cinnamaldehyde using the 2nd generation Hoveyda-Grubbs complex (HG) as catalyst, either dissolved in toluene or supported on silica. Reactions were carried out in batch reactors between 313 and 343 K. The yield to cross-metathesis products (Y_{C-M}) for the MO cross-metathesis with cinnamitrile and cinnamaldehyde increased with the initial molar reactant ratio ($R_{CN/MO}$, $R_{CA/MO}$), reaching Y_{C-M} values of 82% and 95%, respectively, at $R = 7$. No catalyst deactivation took place during the 400-min catalytic runs. The liquid-phase cross-metathesis of MO with ethylene (ethenolysis) was performed over HG(10%)/SiO₂ catalysts, producing 1-decene and methyl 9-decenoate, a valuable intermediate for the synthesis of pheromones. At $R_{C2/MO} = 2.5$, the selectivity to ethenolysis products was 77% at 82% MO conversion. The MO self-metathesis was the only side reaction observed in all the catalytic tests.

Keywords— oleochemistry, metathesis, Hoveyda-Grubbs catalyst, methyl oleate

I. INTRODUCTION

Within the context of sustainable development and green chemistry, the use of vegetable oils as renewable raw materials for manufacturing processes became increasingly relevant in recent years (Montero de Espi-

nosa and Meier, 2011). High volume productions of oilseed crops drive the search of novel synthetic routes toward value-added products from oil-derived feedstocks such as fatty acid methyl esters (FAME) that can be easily obtained at low cost via triglyceride esterification. Most of oleochemical reactions of FAME are carried out in the carboxy functions, but the synthesis of useful chemical intermediates via reactions of the C=C bond is becoming increasingly attractive at industrial level (Biermann *et al.*, 2011). In particular, the metathesis of FAME with functionalized lower olefins is a field of increasing interest in oleochemistry because the formation of carbon-carbon double bonds allows the synthesis of useful fine chemical and polymer intermediates (Chikkali and Mecking, 2012; Rybak *et al.*, 2008). Elevance Renewable Sciences successfully commercialized natural oil metathesis at scale recently when the company commissioned its biorefinery (180,000 tons per year) in Gresik, Indonesia. Conversion of unsaturated fatty acids and oils via metathesis reactions was clearly improved by the development of Grubbs' Ru alkylidenes and the second-generation Ru Hoveyda-Grubbs (HG) complexes (Trnka and Grubbs, 2001). These Ru complexes are highly tolerant to the nucleophilic functional groups of FAME and exhibit remarkable stability in the presence of moisture and oxygen (Conrad and Fogg, 2006; Vougioukalakis and Grubbs, 2010).

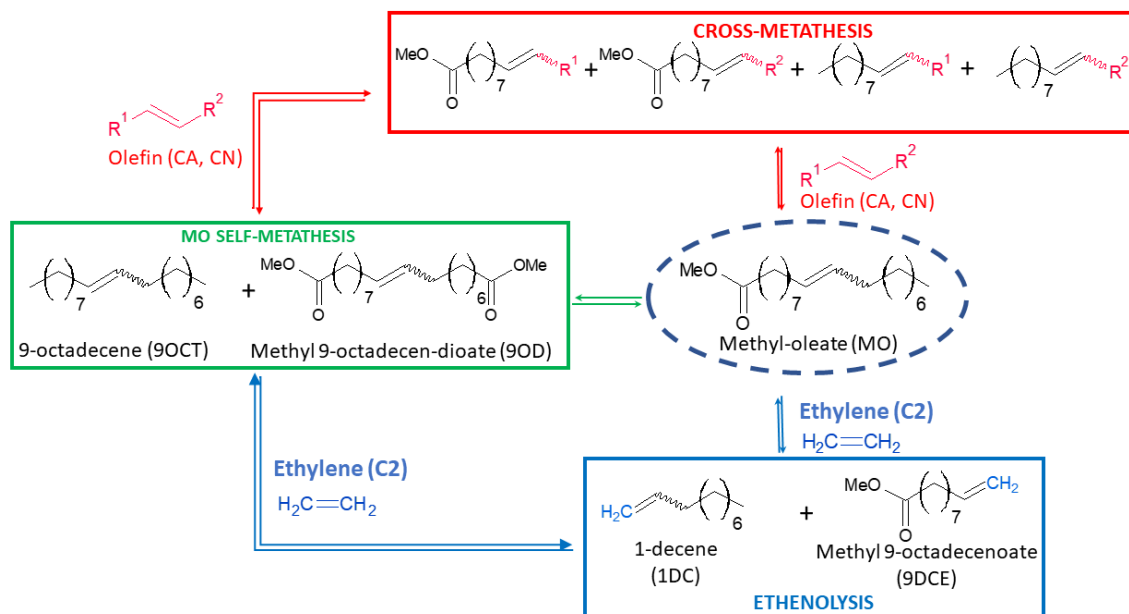


Figure 2: General reaction network for the cross-metathesis of methyl oleate (MO) with ethylene (ethenolysis) and functionalized olefins (CA, CN) (R^1 : phenyl, R^2 : cyano) and CA (R^1 : phenyl, R^2 : formyl)

In this work, we study the catalytic performance of the 2nd generation Hoveyda-Grubbs catalyst (Fig. 1), either dissolved in toluene or supported on silica, for the cross-metathesis of MO with ethylene (C2) and two functionalized olefins: cinnamitrile (CN) and cinnamaldehyde (CA). Ethylene is a widely used feedstock available from petrochemical sources, while CN and CA are terpenoids derived from renewable sources like plant essential oils. Figure 2 presents a general reaction network for the cross-metathesis of MO with C2, CN and CA. The MO/CN and MO/CA reactions produce four cross-metathesis products while MO simultaneously forms, via a parallel reaction pathway, two MO self-metathesis compounds: 9-octadecene (9OCT) and dimethyl 9-octadecen-1,18-dioate (9OD). In the case of MO/C2 reaction, only two products are formed by MO/C2 cross-metathesis: methyl 9-decenoate (9DCE) and 1-decene (1DC). All the products obtained via cross-metathesis reactions in Fig. 2 are valuable fine chemicals. For example, the MO/CA cross-metathesis yields 2-undecenal (2UAL), a fragrance used in cosmetics and perfumery that presents also antibacterial and antifungal activity (Kubo *et al.*, 2003), methyl 10-phenyl-9-decenoate (10DE), an intermediate in polymer manufacture, and 1-decylbenzene (1DB) and methyl 11-oxo-9-undecenoate (11UDE) that are used for the synthesis of biodegradable surfactants. The MO/CN cross-metathesis produces methyl 10-cyano-9-decenoate (10CIA), a polyamide-fiber precursor and 2-undecenenitrile (2UN), an intermediary in the synthesis of long-chain amines used as cationic surfactants. Finally, the MO ethenolysis forms methyl 9-decenoate (9DCE), a very important intermediary in the synthesis of pheromones for ecological pesticides, prostaglandins, fragrances and polymers (Mol, 2002, 1994), while 1DC is a valuable α -olefin with applications as copolymer (Nickel *et al.*, 2012).

II. METHODS

A. Catalyst preparation and characterization

HG(10%)/SiO₂ was prepared by impregnating a commercial SiO₂ (Sigma-Aldrich G62, 230 m²/g, 200 mesh) previously calcined for 2 hr at 773 K, with HG (Sigma-Aldrich, 97%) dissolved in cyclohexane (Sigma-Aldrich, anhydrous, 99.5%) as described elsewhere (Zelin *et al.*, 2013). The Ru content on HG/SiO₂ was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer Optima 2100).

B. Catalytic tests

Cross-metathesis of methyl oleate (Sigma-Aldrich, 99%) with cinnamaldehyde (Aldrich, 99%) or cinnamitrile (Sigma-Aldrich, 97%), was performed in Ar using a Schlenk reactor at atmospheric pressure. The solvent (toluene, Cicarelli, 98%), was dehydrated with metallic Na and benzophenone (Aldrich, 99%). The reactor was loaded with 10 ml of solvent at room temperature, n-dodecane (internal standard, Aldrich, 99%), and variable amounts of MO and CA or CN. The reaction mixture was stirred and heated to the reaction temperature and then a solution of the HG complex in toluene was added to start the reaction.

The cross-metathesis of MO with ethylene (Indura, 5% in N₂) was performed in a 100 ml batch reactor (Parr 4565), loaded with 35 ml of anhydrous cyclohexane (solvent) and 130 mg of HG/SiO₂. After stirring and heating to the reaction temperature, MO dissolved in cyclohexane together with n-dodecane (internal standard) was added to start the reaction after pressuring with the C₂H₄(5%)/N₂ mixture.

In all the catalytic tests, samples were taken periodically from the reactor, quenching the reaction by adding ethanol immediately after extraction. Reaction products

were analyzed by ex-situ gas chromatography (Agilent 6850 GC, FID detector), using an HP-1 capillary column (50 m x 0.32 mm ID x 1.05 μ m film thickness). Identification of product was accomplished by GC-MS in a Thermo Scientific ISQ series unit coupled to a Thermo Scientific Trace 1300 GC equipped with a TR5-MS column (30 m x 0.25 mm x 0.25 μ m film thickness).

Yields of cross-metathesis (Y_{C-M}) or ethenolysis (Y_E) products were calculated in carbon basis, as:

$$Y_{C-M}, Y_E = \frac{\sum_i \alpha_i n_i}{\alpha_{MO} n_{MO}^0}$$

where n_i are the moles of product i , formed from the cross-metathesis reaction, α_i is the number de C atoms from the MO molecule in the product i , n_{MO}^0 are the initial moles of MO in the reactor and α_{MO} is the number of C atoms in the MO molecule). In the same way, the yield of self-metathesis products (Y_{S-M}) was calculated as:

$$Y_{S-M} = \frac{\sum_j \alpha_j n_j}{\alpha_{MO} n_{MO}^0}$$

where n_j are the moles of product j formed from the self-metathesis reaction and α_j is the number de C atoms from the MO molecule in the product j .

The selectivities of cross- and self-metathesis products were obtained from:

$$S_{C-M} = Y_{C-M}/X_{MO}; S_{S-M} = Y_{S-M}/X_{MO}$$

where X_{MO} is the conversion of MO.

III. RESULTS

A. Cross-metathesis of MO with cinnamonnitrile

Figure 3 shows the evolution of conversions (X_{MO} , X_{CN}) and yields to MO/CN cross-metathesis (Y_{C-M}) and MO self-metathesis (Y_{S-M}) products with the progress of the reaction obtained at reactant molar ratio $R_{CN/MO}=1$. MO was rapidly converted to self-metathesis products,

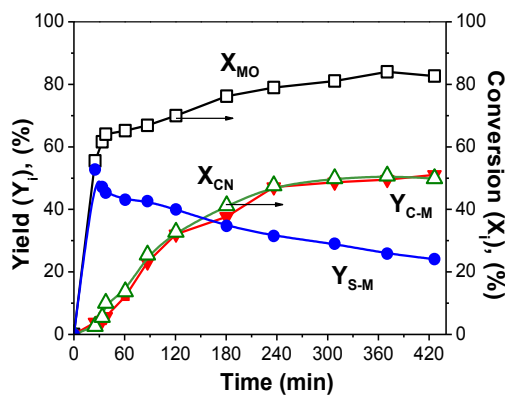


Table 1. Cross-metathesis of MO with cinnamonnitrile: Catalytic results

$R_{CN/MO}$	X_{MO}^a (%)	X_{MO}^{eq} (%)	X_{CN}^a (%)	Y_{C-M}^a (%)
1	81	79	53	53
3	86	89	23	59
5	95	94	20	83
7	97	96	12	84

^a At the end of catalytic runs

T = 343 K, $C_{MO}^0 = 0.0145$ M, $W_{HG} = 2.24$ mg, $HG/MO = 1.19$

9OCT and 9OD, that then went through a maximum because they react with CN to form cross-metathesis products as depicted in Fig. 2. These results reveal that the MO conversion rate by self-metathesis is significantly faster than by cross-metathesis with cinnamonnitrile. On the other hand, no formation of CN self-metathesis products was detected which is consistent with previous work reporting that the self-metathesis of unsaturated nitriles is hardly promoted by Grubb's Ru complexes (Miao *et al.*, 2011). The curves in Fig. 3 show that when the reaction system reached the equilibrium at $X_{MO} = 0.81$, the Y_{C-M} and Y_{S-M} values were 53 and 26%, respectively. Metathesis reactions are limited by the thermodynamic equilibrium (Grubbs, 2003). To improve the yield to cross-metathesis products, additional catalytic tests were therefore carried out by increasing the CN concentration since the reaction equilibrium is shifted to higher MO conversions when $R_{CN/MO}$ is increased. Table 1 shows quantitative results obtained at the end of the catalytic runs performed at $R_{CN/MO}$ between 1 and 7; in all the cases the initial MO concentration (C_{MO}^0) was 0.0145 M. Table 1 also includes the values of the theoretical MO equilibrium conversions (X_{MO}^{eq} , column 3) that were determined from the experimental equilibrium data obtained at $R_{CN/MO} = 1$ in Fig. 3 and using a method reported elsewhere (Nieres *et al.*, 2018). Data in Table 1 show that X_{MO} increased from 81% at $R_{CN/MO} = 1$ to 97% at $R_{CN/MO} = 7$; these experimental X_{MO} values were similar to the corresponding X_{MO}^{eq} values, which indicates that the MO/CN cross-metathesis reaction is not inhibited using high CN concentrations. The yield to cross-metathesis products, Y_{C-M} , increased from 53% ($R_{CN/MO} = 1$) to 84% ($R_{CN/MO} = 7$) at the expense of Y_{S-M} ; consistently, S_{C-M} increased from 65 to 86% when $R_{CN/MO}$ was varied from 1 to 7. In all the cases, carbon balances were close to 100%, thereby excluding the presence of side reactions not considered in the reaction network depicted in Fig. 2.

The initial CN conversion (r_{CN}^0 , mmol/h g) and cross-metathesis products formation (r_{C-M}^0) rates were determined from X_{CN} and Y_{C-M} vs t curves obtained at different $R_{CN/MO}$ ratios by polynomial regression and numerical differentiation extrapolated to zero time; results are presented in Table 2. The r_{C-M}^0 values corresponded approximately to $2r_{CN}^0$ as predicted from the reaction pathways in Fig. 2. Besides, Table 2 shows that r_{CN}^0 increased with $R_{CN/MO}$ suggesting that MO/CN cross-metathesis is positive order with respect to CN. It is worth noting that the r_{C-M}^0 values in Table 2 are significantly lower than those reported in literature for the metathesis of MO with linear unsaturated nitriles such as 3-pentenitrile (Nieres *et al.*, 2016a), probably reflecting a steric hindrance of the phenyl group for the coordination of CN with the Ru active center of HG

Table 2: Kinetic data for MO/CN cross-metathesis

$R_{CN/MO}$	r_{CN}^0 (mol/h g)	r_{C-M}^0 (mol/h g)
1	51	82
3	50	90
5	74	143
7	79	157

Reaction conditions: see Table 1

catalyst.

B. MO cross-metathesis with cinnamaldehyde

The cross-metathesis of FAME with α,β -unsaturated aldehydes such as cinnamaldehyde (CA) is an attractive synthesis route for obtaining valuable chemicals because the formyl group provides direct access to various organic functionalities. Cinnamaldehyde is a natural product that occurs in the bark of cinnamon trees and represents about 60-70% of the essential oil of cinnamon. The products formed from the cross-metathesis of FAME with cinnamaldehyde may be fully obtained then

cient 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 (Fleckhaus *et al.*, 2019). Nevertheless, the industrial application of homogeneous olefin metathesis catalysts is hampered by the difficulties associated with removing Ru from the reaction media and the expensive separation/recovery steps required to obtain high-purity products. Thus, the development of efficient processes using solid catalysts is a highly desirable technological target for the metathesis of oil-derived

Table 3. Cross-Metathesis of MO with cinnamaldehyde. Catalytic results

$R_{CA/MO}$	X_{MO}^a (%)	X_{MO}^{eq} (%)	X_{CA}^a (%)	Y_{C-M}^a (%)	Y_{S-M}^a (%)	S_{C-M}^a (%)	S_{S-M}^a (%)	Carbon Balance ^a (%)
1	79	80	50	52	26	67	33	99
3	91	91	29	80	10	89	11	99
5	96	96	19	91	5	95	5	100
7	97	97	11	95	2	98	2	99
10	100	100	9	100	0	100	0	100

^a At the end of catalytic runs

T = 323 K, $C_{MO}^0 = 0.0145$ M, $W_{HG} = 2.24$ mg, $HG/MO = 1.19\%$ molar, solvent: toluene

from bio-renewable raw materials. The cross-metathesis of MO with cinnamaldehyde was carried out at 323 K in toluene using $R_{CA/MO}$ ratios between 1 and 10 for $C_{MO}^0 = 0.0145$ M. Table 3 presents the values of MO conversions, yields, selectivities, and carbon balances determined at the end of the runs. X_{MO} increased from 79% at $R_{CA/MO} = 1$ to 100% at $R_{CA/MO} = 10$. On the other hand, Y_{C-M} increased from 52% ($R_{CA/MO} = 1$) to 100% ($R_{CA/MO} = 10$) at the expense of Y_{S-M} ; consistently, S_{C-M} increased from 67 to 100% when $R_{CA/MO}$ was varied from 1 to 10. The carbon balance was close to 100% in all the cases, which indicates that HG was highly selective for the formation of self- and cross-metathesis products. In summary, data in Table 3 show that the HG complex was a very efficient catalyst for the MO/CA cross-metathesis that yields 100% of the cross-metathesis products at 323 K and $R_{CA/MO} = 10$.

C. MO cross-metathesis with ethylene (ethenolysis)

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 effi-

functionalized olefins. 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. Here, we investigate the ethenolysis of methyl oleate on $HG(10\%)/SiO_2$ in cyclohexane at 313 K and using $R_{C_2/MO}$ ratios between 1.2 and 3.0. It is important to note that Ru leaching may be significant if heterogeneous catalysts prepared by soft adsorption (impregnation) of the Ru complex on the support are used in polar solvents for the metathesis of functionalized olefins such as FAME. In this regard, we verified here that there is not lixiviation of the HG complex when cyclohexane is used as the solvent, in agreement with results reported by other authors [Van Berlo *et al.*, 2008]. Table 4 shows the catalytic results obtained for MO ethenolysis at $C_{MO}^0 = 0.011$ mol/L and different $P_{C_2H_4}$. The yield to ethenolysis products (Y_E) increased from 52% at $R_{C_2/MO} = 1.2$ to 63% at $R_{C_2/MO} = 2.5$, while S_E augmented from 69% to 77% when $R_{C_2/MO}$ was varied between 1.2 and 2.5. On the other

Table 4. Cross-metathesis of MO with ethylene: Catalytic results.

$R_{C_2/MO}$	X_{MO}^a (%)	X_{MO}^{eq} (%)	Y_E^a (%)	Y_{S-M}^a (%)	S_E^a (%)	S_{S-M}^a (%)	Carbon Balance ^a (%)
1.2	76	76	52	24	69	31	100
2.0	78	78	57	21	73	27	99
2.5	82	82	63	20	77	23	100
3.0	78	87	57	21	73	27	98

^a At the end of catalytic runs.

T = 313 K, $C_{MO}^0 = 0.0145$ M, $P_T = 2-6$ bar, Catalyst: $HG(10\%)/SiO_2$, $W_{cat} = 130$ mg, solvent: cyclohexane.

hand, Table 4 shows that X_{MO} was 82% for $R_{C_2/MO}=2.5$, reaching the X_{MO}^{Eq} value. However, at $R_{C_2/MO}=3.0$ the X_{MO} value was only 78%, significantly lower than that corresponding to X_{MO}^{Eq} (87%), which suggests that the ethenolysis of MO is inhibited at high ethylene concentrations. In summary, results in Table 4 show that HG/SiO₂ catalyst efficiently promotes the cross-metathesis of MO with ethylene and the yield to ethenolysis products increases with $R_{C_2/MO}$ ratio because the equilibrium is shifted to high MO conversions and suppresses the MO self-metathesis competitive reaction. However, deactivation of HG/SiO₂ catalysts also increases with the ethylene/MO ratio.

D. Catalyst stability

According to literature, terminal olefins may deactivate Grubbs complexes in cross-metathesis reactions because of the formation of unstable methylidene intermediates leading to hydride species that suppress the metathesis cycle [Hong *et al.*, 2003]. Here, we investigate the HG stability for MO cross-metathesis with two

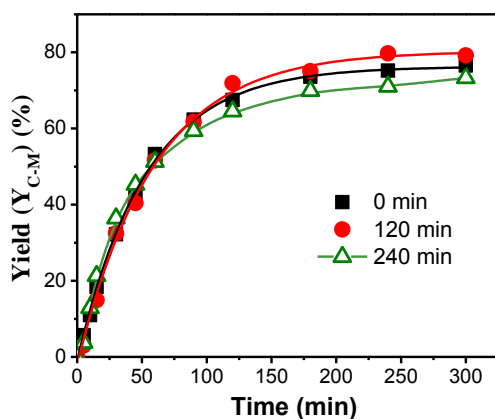


Figure 4: MO/CN cross-metathesis. Y_{CM} vs t curves obtained after 0, 120 and 240 min of CN-HG contact time [T=343 K, $C_{MO}^0=0.0145$ M, $R_{CN/MO}=5$, $W_{HG}=2.24$ mg, $HG/MO=1.19\%$ molar, solvent: toluene]

internal (CN, CA) and one terminal (C2) olefins. In the case of MO/CN cross-metathesis, CN and HG complex were contacted at 343 K for increasing times before the addition of methyl oleate to start the cross-metathesis reactions. In Fig. 4 we plotted the evolution of Y_{CM} with the progress of the reaction after contacting CN with HG for 0, 120 and 240 min. The three Y_{CM} vs t curves were very similar suggesting that the previous contact between CN and HG did not inhibit the catalytic performance of HG complex.

The stability of HG complex for the MO/CA cross-metathesis reaction was studied at 323 K and $R_{CA/MO}=10$ by performing three consecutive catalytic tests without stopping the run. The following procedure was employed: i) the first catalytic cycle was carried out until MO was completely converted and the yield to cross-metathesis products, Y_{C-M} , reached 100%; ii) then, we introduced to the reactor the amounts of MO and CA

required for obtaining the initial MO and CA concentrations, and performed a second consecutive catalytic cycle until X_{MO} reached again 100%; iii) a third consecutive catalytic cycle was carried out following the same procedure. Table 5 shows the values of the initial for-

Table 5. MO/CA cross-metathesis. HG stability for three consecutive catalytic runs

Run	r_{C-M}^0 (mol/h g)	Y_{C-M}^a
1	0.005	103
2	0.004	103
3	0.005	100

^aAt the end of catalytic runs

[T=323 K, $C_{MO}^0=0.00725$ M, $R_{CA/MO}=5$, $W_{HG}=3.36$ mg, solvent: toluene]

mation rate of cross-metathesis products (r_{M-C}^0 , mmol/h g) and Y_{C-M} obtained for the three catalytic cycles. It is observed that the respective values of r_{M-C}^0 and Y_{C-M} were similar for the three catalytic cycles, thereby indicating that the in-situ deactivation of HG with the progress of the reaction was negligible.

Finally, the effect of contacting ethylene with HG(10%)/SiO₂ at increasing times previously to perform

the MO/C2 cross-metathesis reaction was studied at 313 K and $P_{C_2H_4}=0.250$ bar. Specifically, HG(10%)/SiO₂ was in contact with ethylene in cyclohexane (solvent) for 0 min, 15 min, and 30 min before adding methyl oleate to start the reaction. Table 6 presents the values of r_E^0 , the initial formation rate of ethenolysis products, and Y_E , the yield to ethenolysis

Table 6. Catalyst stability for MO ethenolysis

C2-HG contact time (min)	r_E^0 (mol/h g)	Y_E^a (%)
0	0.0015	60
15	0.0008	43
30	0.0005	25

^aAt the end of the runs

[Catalyst: HG(10%)/SiO₂, T=313 K, $P_{C_2H_4}=0.250$ bar, $P_T=5$ bar, $C_{MO}^0=0.011$ M, $R_{C_2/MO}=2.5$, $W_{cat}=130$ mg, Solvent: cyclohexane]

products. Both parameters, r_E^0 and Y_E , clearly diminished as the contact period between ethylene and HG(10%)/SiO₂ was increased, which confirms that the ethylene/catalyst interaction may inhibit the catalytic ability of promoting ethenolysis reactions. The deactivation of HG complex in the presence of ethylene and terminal olefins has also been observed in previous work and was attributed to formation of unstable methylidene intermediates leading to hydride species that suppress the metathesis cycle (van Rensburg *et al.*, 2004, Zelin *et al.*, 2015).

IV. CONCLUSIONS

The cross-metathesis of oil-derived methyl oleate (MO) with cinnamitrile (CN), cinnamaldehyde (CA) and ethylene (C₂) represents an attractive route to produce valuable chemical compounds from renewable resources. Here, the 2nd generation Hoveyda-Grubbs catalyst (HG) dissolved in toluene efficiently promoted the MO cross-metathesis with CN and CA, yielding 84% and 100% of cross-metathesis products, respectively, for $R_{CN/MO}=7$ and $R_{CA/MO}=10$ reactant ratios. The yield to cross-metathesis products increased with $R_{CN(CA)/MO}$ ratios because the equilibrium is shifted to high MO conversions and suppresses the MO self-metathesis competitive reaction.

The cross-metathesis of MO with ethylene was carried out in cyclohexane at different ethylene pressures, using HG/SiO₂ solid catalysts and slurry batch reactors. In all the cases, it was verified that no Ru leaching from the catalyst took place by using cyclohexane as solvent. The catalyst performance increased with $R_{C_2/MO}$ ratio, but the highest values of yield ($Y_E = 63\%$) and selectivity ($S_E = 77\%$) to ethenolysis products were obtained at $R_{C_2/MO} = 2.5$, because the reaction was markedly inhibited for $R_{C_2/MO}$ values higher than 2.5.

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