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Heterogeneous catalysis for valorisation of vegetable oils via metathesis reactions: Ethenolysis of methyl oleate

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The cross-metathesis of methyl oleate (MO) with ethylene was studied on the second-generation Hoveyda-Grubbs complex supported on silica (HG/SiO$_2$). The reaction was carried out in a batch slurry reactor at 313-353 K and 2.5-7.5 bar of C_2H_4(5%)/N_2, using cyclohexane as solvent. The MO ethenolysis products were methyl 9-decenoate and 1-decene. Competitive MO self-metathesis reaction formed 9-octadecene and methyl 9-octadecen-1,18-dioate. The yield (Y_E) and selectivity (S_E) to ethenolysis products at $P_{C_2H_4}$= 0.125 bar (total pressure = 2.5 bar) were 52% and 69%, respectively. Both parameters increased with $P_{C_2H_4}$, essentially because the reaction equilibrium was shifted to higher methyl oleate conversions. Thus, at $P_{C_2H_4}$= 0.250 bar, the Y_E and S_E values were 63% and 77%, respectively. Nevertheless, catalyst deactivation was observed for ethylene pressures higher than 0.125 bar, thereby suggesting that the presence of ethylene may suppress the metathesis cycle on HG/SiO$_2$ catalysts. The yield to ethenolysis products decreased when the temperature was increased, reflecting mainly the MO equilibrium conversion diminution.

1- Introduction

Fatty acid monoesters (FAME), such as methyl oleate (MO), are cheap feedstocks derived from transesterification of seed oils and fats with a lower alcohol. Industrial valorisation of FAME via reactions in the carboxy function has already occurred in several areas, but the synthesis of chemicals by reactions of the C=C bonds is becoming progressively attractive.[1-3] In particular, the catalytic metathesis of FAME is a field of increasing interest in oleochemistry because the formation of carbon–carbon double bonds allows the synthesis of useful value-added chemical and polymer intermediates.[4,5] Conversion of unsaturated fatty acids and oils has been widely studied using homogeneous catalysis, in particular Grubbs' Ru alkylidenes and the second-generation Ru Hoveyda-Grubbs (HG) complex (Fig. 1) that exhibit high activity and remarkable stability to the presence of moisture and oxygen.[6-9] Nevertheless, the industrial use of homogeneous catalysis for FAME metathesis is hindered by the costly catalyst separation and recovery steps required to yield high-purity chemicals as well as by the product contamination by Ru catalyst residues. There is a need then to develop active and selective immobilized supported complexes that would allow straightforward catalyst separation and recovery. However, very few papers on the use of supported Ru complexes for FAME metathesis have been published, probably because they frequently suffer from leaching or losses of activity as a result of the complex immobilization. Several papers have recently shown that Ru–alkylidene complexes immobilized on silica, MCM-41 and SBA supports can be employed without leaching in some solvents for olefin metathesis reactions.[10-13] Regarding FAME metathesis, we have recently reported that the self-metathesis of MO and the cross-metathesis of MO with 1-hexene are efficiently promoted on silica-supported HG complexes, without HG leaching when using cyclohexane as solvent. [14,15]

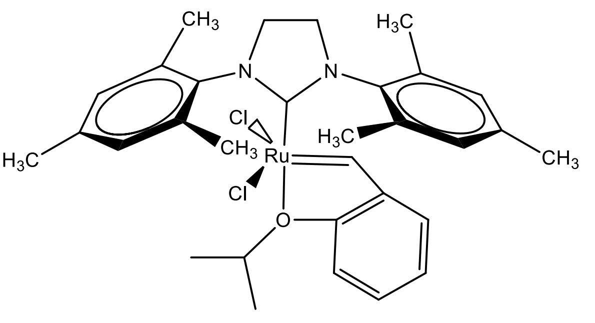

Fig 1 Second-generation Ru Hoveyda-Grubbs catalyst

The cross-metathesis of FAME with simple non-functionalized alkenes like ethylene, 2-butene and 1-hexene has been investigated to obtain less abundant medium-chain fatty acid esters that are valuable intermediates in fine chemistry.[16-18] The cross metathesis of

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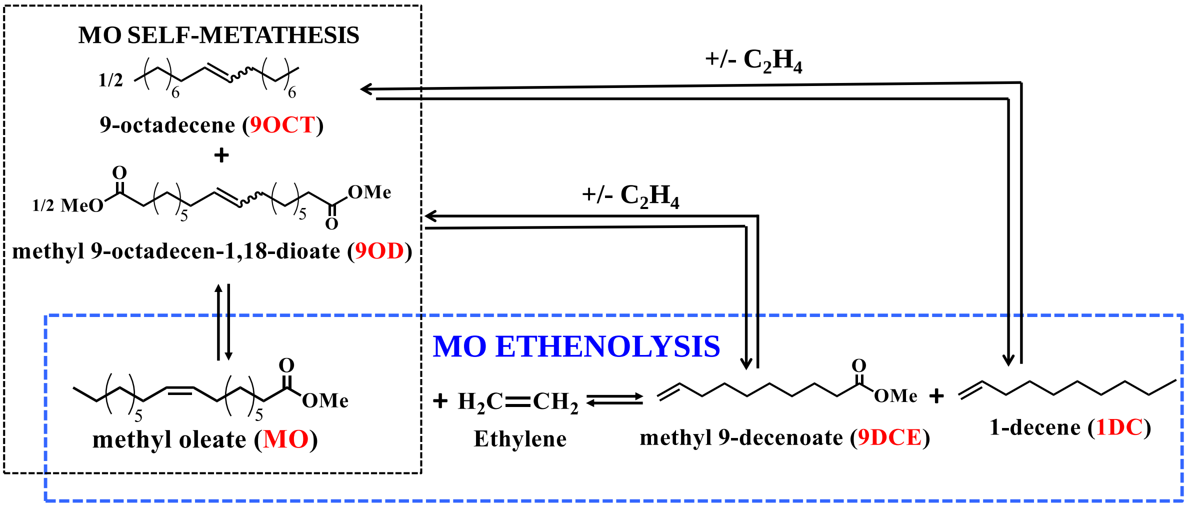
ethylene has received special attention for a long time since this process allows the synthesis of 1-olefins, which have broad range of applications in polymer industry.[19] Bradshaw et al. were the first to recognize the great potential of this reaction for splitting internal olefins into molecules of 1-olefin and called it "ethenolysis".[20] In particular, the ethenolysis of methyl oleate has been investigated essentially on homogeneous Ru-based complexes.[21-24] In heterogeneous catalysis, the ethenolysis of MO was studied on Re_2O_7/Al_2O_3 and on CH_3ReO_3 supported on SiO_2-Al_2O_3[25,26], but there are no reports on the use of immobilized Ru complexes for promoting this metathesis reaction. Precisely, in this work we investigate the ethenolysis of MO on silica-supported second generation Ru Hoveyda-Grubbs complex. The cross-metathesis of MO with ethylene produces methyl 9-decenoate (9DCE) and 1-decene (1DC), as depicted in Scheme 1. 9DCE is a valuable intermediate for the synthesis of 9-oxo-trans-2-decenoic acid, a honeybee pheromone (the queen substrate). Pheromones are non-toxic and biodegradable chemicals increasingly employed for the control of insect pests.[27] The pheromone synthesis via metathesis reactions is an alternative technology to the current processes involving multistep sequences.[28] 9DCE is also employed in perfumery, and for the synthesis of prostaglandins and a number of polymers and co-polymers.[29,30] In addition, 1-decene is a valuable α-olefin that is used as a monomer in copolymers as well as in surfactants, lubricants and epoxides.[31] The self-metathesis of MO that produces 9-octadecene (9OCT) and dimethyl 9-octadecen-1,18-dioate (9OD) is the main secondary reaction in the MO ethenolysis reaction network (Scheme 1). 9OCT and 9OD may in turn react with ethylene to form the ethenolysis products. In this work, we show that HG/SiO_2 catalysts promote efficiently the ethenolysis of methyl oleate, and no HG leaching takes place using cyclohexane as solvent. The yield and selectivity to ethenolysis products increase with the ethylene pressure, essentially because the reaction equilibrium is shifted to higher methyl oleate conversions.



Scheme 1: Reaction network of ethenolysis of methyl oleate

2- Material and Methods

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2.1. Catalyst preparation and characterization

HG/SiO_2 samples containing up to 10 wt.% HG (Sigma-Aldrich, 97%) were prepared by impregnating a commercial silica (Sigma-Aldrich G62, 230 m^2/g, 200 mesh) previously calcined 2 h at 773 K with a solution of HG in anhydrous cyclohexane. The silica impregnation was carried out at 298 K by stirring during 30 min; the solid colour rapidly changed from white to green and was then filtered and dried in vacuum. The Ru content in HG/SiO_2 samples was determined by measuring by UV-vis spectroscopy (Perkin-Elmer Lambda 20 spectrophotometer) the colorimetric difference of the HG impregnating solution, before and after impregnation. The presence of Ru in the liquid phase was investigated by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using a Perkin–Elmer Optima 2100 unit. The solid crystalline structures were determined by X-ray diffraction (XRD) in the range of 2θ = 5-50º, using a Shimadzu XD-D1 diffractometer and Ni-filtered Cu Kα radiation (λ = 1.540 Å).

The samples were characterized by Fourier transform infrared spectroscopy (FTIR) in the 500-800 cm^{-1} region using a Shimadzu Prestige 21 spectrophotometer. The spectral resolution was 4 cm^{-1} and 140 scans were added. Powder samples were mixed with KBr and pressed to thin wafers. Spectra were taken at room temperature by subtracting the background spectrum recorded previously.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were carried out in a Shimadzu IR Prestige-21 spectrophotometer, equipped with an in-situ high-temperature/high pressure SpectraTech cell and a liquid nitrogen-cooled MCT detector. The sample holder was placed inside a dome with CaF_2 windows. The DRIFT spectra were collected in Ar (60 ml/min). The spectrum of silica support was previously collected. The IR spectra showed in this paper for HG/SiO_2 samples are the difference spectra where the SiO_2 spectrum served as the reference.

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2.2. Ethenolysis of methyl oleate

The cross-metathesis of methyl oleate (Sigma-Aldrich, 99%) with ethylene (Indura, 5% in N_2) was carried out in a batch reactor of 100 ml (Parr 4565) at 2.5-7.5 bar and 313-353 K. Anhydrous cyclohexane (Sigma-Aldrich, 99.5%) was used as solvent. In a typical experiment, the reactor was loaded at room temperature with cyclohexane (35 ml) and 130 mg of catalyst and purged under N_2. The mixture was stirred and heated to the reaction temperature in a thermostatic bath, and then MO dissolved in cyclohexane together with n-dodecane (internal standard, Sigma-Aldrich, >99%) were added to start the reaction after pressuring with $C_2H_4(5\%)/N_2$. Reaction products were analyzed by ex-situ gas chromatography in an Agilent 6850 GC chromatograph equipped with a flame ionization detector and a HP-1 capillary column (50 m × 0.32 mm ID, 1.05 µm film). Samples from the reaction system were collected periodically for 60-300 min. Product identification was carried out by mass spectrometry using a Thermo Scientific Trace ISQ QD mass spectrometer coupled with a Thermo Scientific Trace 1300 gas chromatograph equipped with a TR 5MS column (30 m x 0.25 mm x 0.25 µm film thickness). Besides the formation of ethenolysis products (9DCO, 1DC), the production of 9OD and 9OCT from the self-metathesis of MO took place. Yields were calculated in carbon basis. The yield of ethenolysis products (Y_E, C atoms of MO in ethenolysis products/C atoms of MO fed) was determined as $Y_E = \sum \alpha_i\, n_i / \alpha_{MO} n_{MO}^0$, where n_i are the moles of product *i* formed from the cross-metathesis reaction, α_i the number of C atoms of MO in the product *i* molecule, n_{MO}^0 the initial moles of MO, and α_{MO} the number of C atoms in the MO molecule. The yield of MO self-metathesis products was obtained as $Y_{S-MO} = \sum \alpha_j\, n_j / \alpha_{MO} n_{MO}^0$, where n_j are the moles of product *j* formed from the MO self-metathesis reaction and α_j number of C atoms in the product *j* molecule. The selectivity to ethenolysis products was obtained as $S_E = Y_E / X_{MO}$, where X_{MO} is the conversion of MO; similarly, the selectivity to MO self-metathesis products was calculated as $S_{S-MO} = Y_{S-MO} / X_{MO}$

3- Results and Discussion

3.1 Catalyst characterization

Fig. 2 shows the XRD patterns of HG complex[32], silica, and HG/SiO_2 samples containing 6.0 and 10.0% HG. The HG monolayer value on the silica support used in the present work is 11.6%.[14] The diffractograms of HG/SiO_2 samples presented only the amorphous halo of silica support. The absence of diffraction peaks attributable to the HG crystalline structure suggests that the HG complex is highly dispersed on the silica support. Consistently, in a previous work we investigated the cross-metathesis of MO with 1-hexene on HG/SiO_2 catalysts containing different HG loadings and observed that in all the cases the HG complex was entirely accessible and active for carrying out the catalytic reaction.[15]

The interaction between the HG complex and the support was investigated by IR spectroscopy. Fig. 3 shows the FTIR spectra of HG complex, SiO_2, HG(6%)/SiO_2 and HG(10%)/SiO_2 obtained in the 500-800 cm^{-1} region. The HG complex exhibited the 748 cm^{-1} band arising from the Ru=C bond stretch, and the absorption band at 580 cm^{-1} characteristic of the Ru=C vibration.[33] The HG/SiO_2 samples in Fig. 3 also exhibited the IR bands at 748 and 580 cm^{-1} which suggests that the HG structure was conserved after the HG impregnation on the support.

HG(6%)/SiO_2 and HG(10%)/SiO_2 samples together with the HG complex were also characterized by DRIFT spectroscopy. The spectra obtained at 303 K in the 1000-3500 cm^{-1} zone, are presented in Fig. 4. The main absorption bands of the HG complex appeared in the 1200–1700 cm^{-1} and 2800–3200 cm^{-1} regions, in agreement with previous reports.[34] The bands at 1454 cm^{-1}, 1392 cm^{-1} and 1298 cm^{-1} correspond to *ν*(C=C) aromatic, δ(CH_3) and δ(CH_2), respectively. In the 2800–3200 cm^{-1} zone, the IR bands at 2945 cm^{-1} and 2976 1200–1700 cm^{-1} and 2800–3200 cm^{-1} regions, in agreement with previous reports.[34] The bands at 1454 cm^{-1}, 1392 cm^{-1} and 1298 cm^{-1} correspond to *ν*(C=C) aromatic, δ(CH_3) and δ(CH_2), respectively. In the 2800–3200 cm^{-1} zone, the IR bands at 2945 cm^{-1} and 2976 cm^{-1} are attributable to *ν*(CH_3, CH_2) asymmetric and ν(CH_3, CH_2) symmetric stretches. The spectra of HG/SiO_2 samples in Fig. 4 exhibited the main absorption bands of the HG complex, thereby confirming that the

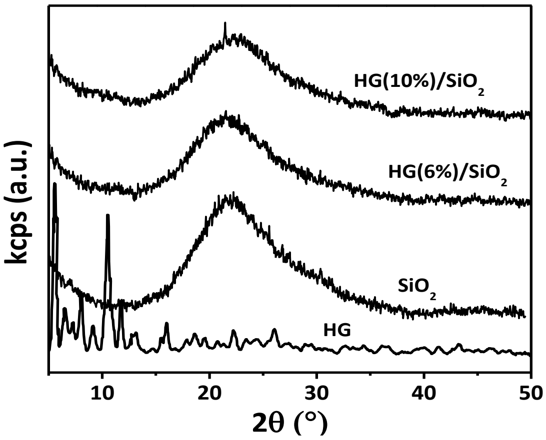

Fig 2 X-Ray diffraction patterns of the HG complex, SiO_2 and HG/SiO_2 samples

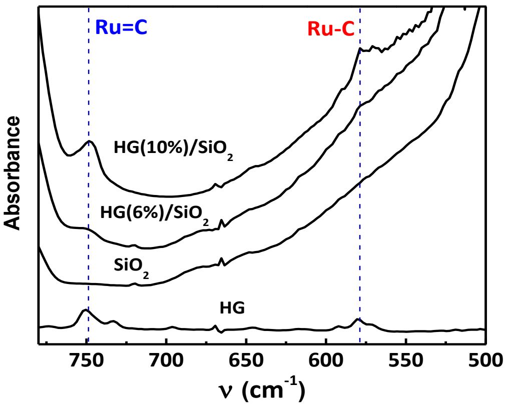

Fig 3 FTIR spectra of the samples in the 500-800 cm^{-1} region

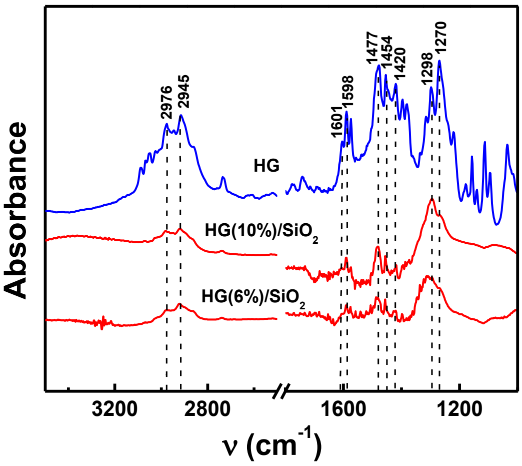

Fig 4 DRIFT spectra of HG complex and HG/SiO$_2$ samples

HG ligands and structure were preserved after the HG deposition on silica.

3.2 Catalytic results

In order to gain insight into the catalytic performance of silica-supported HG catalysts for the ethenolysis of methyl oleate, we initially compared the activity and selectivity obtained on HG(10%)/SiO$_2$ with those achieved by homogeneous catalysis, using dissolved HG complex. The results obtained at 313 K, 2.5 bar of total pressure, and by loading the reactor with the same amount of HG complex, are shown in Fig. 5. By homogeneous catalysis, the MO equilibrium conversion (76%) was rapidly reached after 80 min reaction as well as the equilibrium values for ethenolysis (Y_E = 52%) and MO self-metathesis products (Y_{MO} = 24%). On HG(10%)/SiO$_2$, the reaction equilibrium was achieved after about 180 min reaction, thereby showing that the MO ethenolysis reaction rate diminished when the HG complex was immobilized on silica. Quantitatively, we determined from Fig. 5 that the initial formation rates of ethenolysis products (r_E^0, mmol ethenolysis products/h g_{HG}) were 38 mmol/h g_{HG} on HG(10%)/SiO$_2$ and 61 mmol/h g_{HG} when using dissolved HG complex. These results show that the HG complex loses activity for MO ethenolysis when is supported on silica, which is consistent with what we observed when HG/SiO$_2$ catalysts were employed to promote the self-metathesis of MO.[14] It is worth noting here that we have verified in previous work that there is not leaching of the HG complex in MO metathesis reactions carried out in cyclohexane[14,15] in agreement with results reported elsewhere[10]. In this work, we did not detect the presence of Ru in the liquid phase after our catalytic runs (analysis performed by ICP technique; detection limit: 0.2 ppm Ru). In other words, the data reported here for HG/SiO$_2$ catalysts effectively reflect the activity of immobilized HG complex.

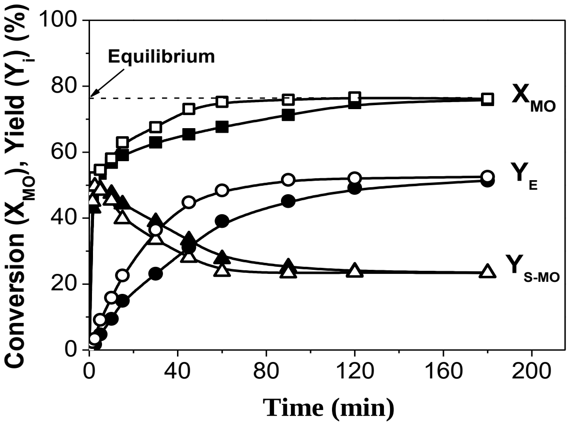

Fig 5 Ethenolysis of methyl oleate using dissolved HG complex (open symbols) and HG(10%)/SiO$_2$ (closed symbols). [T = 313 K, $P_{C_2H_4}$ = 0.125 bar, C_{MO}^0 = 0.011 M, HG = 13 mg, HG(10%)/SiO$_2$ = 130 mg]

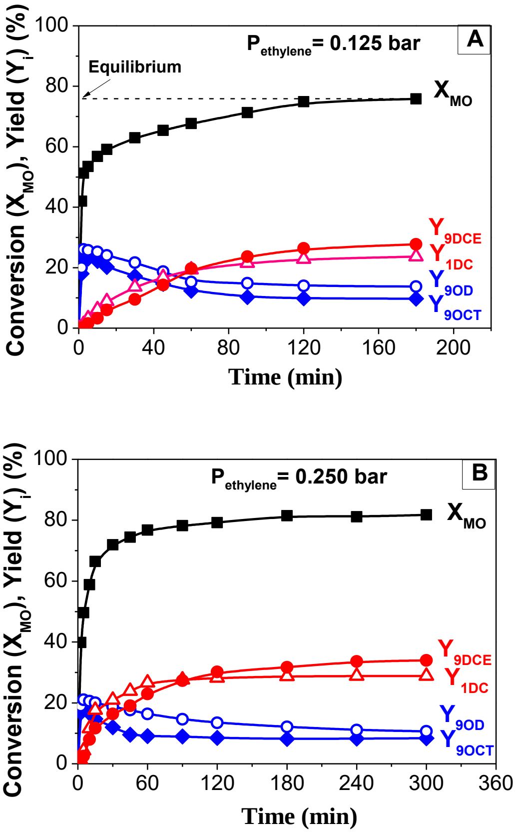

Fig. 6 Ethenolysis of methyl oleate: Efect of $P_{C_2H_4}$. [T = 313 K, C_{MO}^0 = 0.011 M, HG(10%)/SiO$_2$ = 130 mg, solvent: cyclohexane]

In Fig. 6A we plotted the curves of MO conversion (X_{MO}), and yields to ethenolysis (Y_{9DCE}, Y_{1DC}) and MO self-metathesis (Y_{9OD}, Y_{9OCT}) products as a function of time, obtained at 313 K and $P_{C_2H_4}$ = 0.125 bar (P_T = 2.5 bar). We did not detect any products resulting from isomerization or other secondary reactions. Initially, MO was essentially converted to self-metathesis products 9OD and 9OCT that

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Table 1 Catalytic results for ethenolysis of methyl oleate

Total pressure	Ethylene pressure	Reactant ratio	Conversion [a]	Equilibrium conversion	Yield [a]						Selectivity [a]	
P_T (bar)	$P_{C_2H_4}$ (bar)	$R_{C_2H_4/MO}$ [b]	X_{MO} (%)	X_{MO}^{Eq} (%)	Y_{9DCE} (%)	Y_{1DC} (%)	Y_{9OCT} (%)	Y_{9OD} (%)	Y_E (%)	Y_{S-MO} (%)	S_E (%)	S_{S-MO} (%)
2.5	0.125	1.2	76	76	28	24	10	14	52	24	69	31
4.0	0.200	2.0	78	78	31	26	9	12	57	21	73	27
5.0	0.250	2.5	82	82	34	29	8	11	63	20	77	23
6.0	0.300	3.0	78	87	30	27	9	12	57	21	73	27
7.5	0.375	3.7	71	93	24	21	12	14	45	26	63	37

T = 313 K, C_{MO}^0 = 0.011 M, Catalyst: HG(10%)/SiO$_2$, W$_{cat}$ = 130 mg, solvent: cyclohexane

[a] At the end of catalytic runs

[b] Molar ratio

went through a maximum at about 4 min reaction because they react then with ethylene to form ethenolysis products 9DCE and 1DC, as depicted in Scheme 1. These results show that the conversion of MO by self-metathesis reaction is faster than by cross-metathesis with ethylene. The yields to 9DCE and 1DC continuously increased with reaction time up to reach equilibrium at the end of the run. Similarly to other olefin cross-metahesis reactions, the ethenolysis of MO is limited by equilibrium. Here, we determined experimentally the equilibrium data in Fig. 6A by adding fresh catalyst at the end of the reaction to verify that the conversion and yield values were not modified by catalyst addition and thereby confirming that the reaction system was in equilibrium. The equilibrium data corresponding to other reaction temperatures and $P_{C_2H_4}$were obtained in a similar manner.

From the curves of Fig 6A, we determined that the yield to ethenolysis products (Y$_E$) was 52% when equilibrium was reached. In order to improve the Y$_E$ value, we performed additional catalytic tests by increasing the ethylene pressure, taking into account that the reaction equilibrium is shifted to higher MO conversions upon increase of the ethylene/MO reactant ratio ($R_{C_2H_4/MO}$). Specifically, additional runs were carried out at 0.200, 0.250 and 0.375 bar of ethylene. The corresponding concentrations of ethylene dissolved in cyclohexane were determined by using a Henry´s constant of 9.19 bar L/mol[35,36]; the obtained $C_{C_2H_4}$values were 0.0218, 0.0272 and 0.0408 mol/L, respectively. Data in Fig. 6A and Fig. 6B allow to compare the catalytic results obtained at ethylene pressures of 0.125 and 0.250 bar, respectively. Clearly, formation of ethenolysis products increased with $P_{C_2H_4}$ at the expense of MO self-metathesis products.

Quantitative results obtained at C_{MO}^0= 0.011 mol/L and different $P_{C_2H_4}$ are presented in Table 1. Specifically, Table 1 shows the values of MO conversions, yields, and selectivities determined at the end of the runs for $R_{C_2H_4/MO}$ ratios between 1.2 and 3.7. In all the runs, the initial MO/HG molar ratio loaded into the reactor was 21.2 mol MO/mol HG. The MO equilibrium conversion (X_{MO}^{Eq}) increases from 76% at $R_{C_2H_4/MO}$ = 1.2 to 93% at $R_{C_2H_4/MO}$ = 3.7. The MO conversions determined at the end of our catalytic runs reached the X_{MO}^{eq} values for $R_{C_2H_4/MO}$ between 1.2 and 2.5. Consistently, the yield to ethenolysis products (Y$_E$) increased from 52% at $R_{C_2H_4/MO}$= 1.2 to 63 % at $R_{C_2H_4/MO}$ = 2.5. Similar qualitative trend was observed for the selectivity to ethenolysis products, S$_E$, that increased from 69% to 77% when $R_{C_2H_4/MO}$ was varied between 1.2 and 2.5. Nevertheless, the X$_{MO}$ values for $R_{C_2H_4/MO}$ ratios of 3.0 and 3.7 were 78% and 71%, respectively, significantly lower than the corresponding X_{MO}^{Eq} values (85% and 93%), which shows that the ethenolysis of MO is inhibited at high ethylene concentrations. Because of catalyst deactivation, the values of Y$_E$ and S$_E$ at $R_{C_2H_4/MO}$= 3.7 were only 45% and 63%, respectively. In all the cases the carbon balance was close to 100 %, which indicated that HG(10%)/SiO$_2$ is highly selective for the formation of products resulting from ethenolysis and self-metathesis of MO.

In order to stablish the effect of ethylene pressure on the reaction kinetics, we determined the initial formation rate of ethenolysis products (r_E^0, mol/h g$_{HG}$) by calculating the initial slopes from the Y$_E$ vs time curves (see Fig. 5) obtained at different ethylene pressures. The experimental data were interpreted by considering a power-law rate equation:

$$r_E^0 = k(C_{MO}^0)^\alpha (P_{C_2H_4})^\beta \qquad (1)$$

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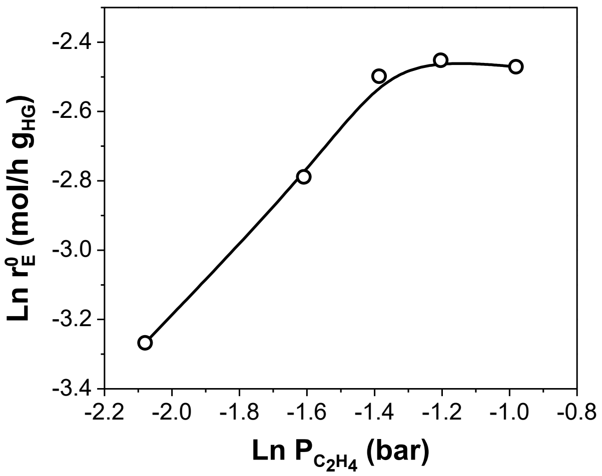

Fig 7 Dependence of the initial formation rate of ethenolysis products upon ethylene pressure [T = 313 K, C_{MO}^0 = 0.011 M, HG(10%)/SiO$_2$ = 130 mg, solvent: cyclohexane]

Fig. 7 shows a plot of ln r_E^0 vs ln $P_{C_2H_4}$. Two regions separated by a $P_{C_2H_4}$ value of approximately 0.250 bar can be distinguished in Fig. 7. The reaction was positive order in ethylene (β ≅ 1.1) in the lower $P_{C_2H_4}$ region, whereas for $P_{C_2H_4}$ > 0.250 bar (i.e. for $R_{C_2H_4/MO}$ > 2.5) the rate did not vary with $P_{C_2H_4}$ (β ≅ 0).

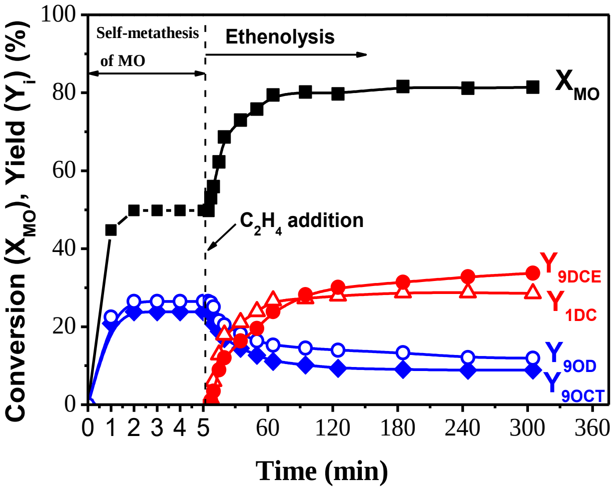

Fig 8 Addition of ethylene following the equilibrium of the MO self-metathesis reaction [HG(10%)/SiO$_2$ = 130 mg, T = 313 K, $P_{C_2H_4}$ = 0.25 bar, C_{MO}^0 = 0.011 M, solvent: cyclohexane]

Table 2: Ethenolysis of methyl oleate: Effect of temperature

T	$C_{C_2H_4}$	r_E^0 [a]	X_{MO} [b]	X_{MO}^{EQ}	Yield [b] (%)		Selectivity [b] (%)	
(K)	(mol/L)	(mmol/h g_{HG})	(%)	(%)	Y_E	Y_{S-MO}	S_E	S_{S-MO}
313	0.0272	82	82	82	63	19	77	23
333	0.0208	249	79	79	57	22	72	28
348	0.0173	472	75	75	54	21	72	28

C_{MO}^0 = 0.011 M, $P_{C_2H_4}$ = 0.25 bar, Catalyst: HG(10%)/SiO$_2$, W_{cat} = 130 mg, solvent: cyclohexane
[a] Initial formation rate of ethenolysis products
[b] At the end of catalytic runs

More insight on the reaction kinetics and mechanism was achieved by carrying out an additional catalytic test at $P_{C_2H_4}$ = 0.250 bar (Fig. 8). The reactor was initially fed only with MO and the self-metathesis reaction proceeded reaching equilibrium. Then, ethylene was added to the reactor and the evolutions of MO conversion, and yields to 9DCE, 1DC, 9OCT and 9OD were followed as a function of time, as shown in Fig. 8. From the curves of Fig. 8 we determined the initial conversion rates of MO, 9OCT and 9OD following the addition of ethylene and obtained: r_{MO}^0 = 31.1 mmol/h g_{HG}, r_{9OCT}^0 = 8 mmol/h g_{HG}, and r_{9OD}^0 = 6.3 mmol/h g_{HG}. We also determined the initial formation rate of ethenolysis products and obtained r_{1DC}^0 = 54.8 mmol/h g_{HG} and r_{9DCE}^0 = 33.2 mmol/h g_{HG}. These results show that the ethenolysis of 9OCT to yield 1DC is faster than 9OD ethenolyis to 9DCE (Scheme 1). On the other hand, we observe that the formation rate of ethenolysis products (r_E^0 = 87.5 mmol/h g_{HG}), is approximately two times the sum of MO, 9OCT and 9OD conversion rates, as predicted by the reaction network in Scheme 1. All these data suggest that the reaction mechanism of ethenolysis of MO on HG(10%)/SiO$_2$ involves initially the rapid MO conversion via MO self-metathesis, followed then by the cross-metathesis of MO, 9OD and 9OCT with ethylene.

The effect of temperature on ethenolysis of MO was investigated in the 313-348 K range at $P_{C_2H_4}$ = 0.250 bar; results are presented in Table 2. The MO equilibrium conversion, X_{MO}^{Eq}, decreased from 82% at 313 K to 75% at 348 K, which reflects the diminution of the dissolved ethylene concentration with temperature.[35,36] As a consequence, the values of the yield and selectivity to ethenolysis products obtained at the end of the runs decreased from 63% (Y_E) and 77% (S_E) at 313 K to 54% and 72% at 348 K, respectively. We also determined the initial formation rate of ethenolysis products; as expected, r_E^0 increased with temperature (Table 2). The *ln*(r_E^0) values from Table 2 were plotted as a function of 1/T for calculating the apparent activation energy, E_{app}, via an Arrhenius-type function (the plot is not shown here). From the slope of the resulting linear plot we obtained E_{app} ≅ 11 kcal/mol.

In summary, the highest values of yield (Y_E = 63%) and selectivity (S_E = 77%) achieved on HG(10%)/SiO$_2$ at 313 K and HG/MO = 4.7 molar% were obtained at $P_{C_2H_4}$ = 0.250 bar (Table 1). Under these reactions conditions, the initial formation rate of ethenolysis products was r_E^0 = 84.2 mmol/h g_{HG} (Fig. 7), or, in terms of turnover frequency, TOF_E^0 = 52.7 h^{-1}. In homogeneous catalysis, the

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ethenolysis of MO on the second-generation Hoveyda-Grubbs complex has been studied only in two papers, using ethylene pressures significantly higher than in the present work.[23,37] At $P_{C_2H_4}$= 20 bar, 303 K and a HG loading of 0.1 mol%, Aydos et al.[37] obtained X_{MO} = 75%, Y_E = 23% and S_E = 31% at the end of 24-h runs; the turnover formation rate of ethenolysis products was TOF_E = 9.7 h^{-1}. Schrodi et al.[23] reported that at $P_{C_2H_4}$= 10 bar, 313 K and 100 ppm of the HG complex, the MO ethenolysis reaches a plateau at 40 min and gives X_{MO} = 60%, Y_E = 20% and S_E = 33%. The low ethenolysis yields obtained in these two papers by homogenous catalysis using the HG complex probably reflect a rapid and complete deactivation of the catalyst. Although high ethylene pressures (> 5 bar) are frequently reported for ethenolysis reactions in order to improve the selectivity to ethenolysis products, the second-generation Hoveyda-Grubbs complex may be rapidly inhibited by the interaction with ethylene, as clearly suggest the data presented in the present work.

Results in Table 1 showed that deactivation of catalyst HG(10%)/SiO$_2$ during the MO ethenolysis reaction becomes significant when $R_{C_2H_4/MO}$ ratios higher than 2.5 are employed (lines 4 and 5). We decided then to explore in more details the effect of ethylene on catalyst deactivation by performing additional catalytic runs for the ethenolysis of MO on HG(10%)/SiO$_2$. Specifically, HG(10%)/SiO$_2$ was contacted with ethylene for increasing times at 313 K and $P_{C_2H_4}$= 0.250 bar before adding methyl oleate to start the ethenolysis reaction. Fig. 9 shows the evolutions of X_{MO} and Y_E with time obtained after contacting HG(10%)/SiO$_2$ with ethylene for 0 min, 15 min, and 30 min before the addition of MO. The X_{MO} and Y_E values obtained at the end of the runs clearly diminished as the contact period between ethylene and HG(10%)/SiO$_2$ was increased, which confirms that the ethylene/catalyst interaction may inhibit the catalyst ability for promoting ethenolysis reactions. Other authors have also observed the Hoveyda-Grubbs complex deactivation in presence of ethylene and terminal olefins, and they attributed the phenomenon to the low stability of methylidene intermediates leading to hydride species that may suppress the metathesis cycle.[38,39]

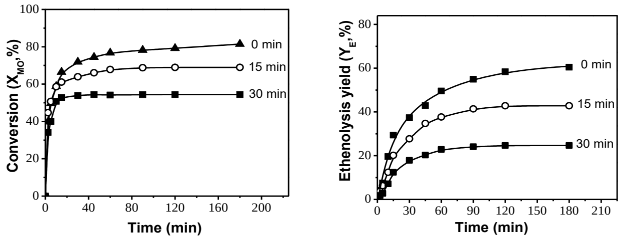

Fig 9 Ethenolysis of MO: Effect of contacting HG(10%)/SiO$_2$ with ethylene before the addition of MO. Contact times: 0 min, 15 min, 30 min. [HG(10%)/SiO$_2$ = 130 mg, T = 313 K, $P_{C_2H_4}$ = 0.250 bar, C_{MO}^0 = 0.011 M, solvent: cyclohexane].

Conclusions

The second-generation Hoveyda-Grubbs complex immobilized on silica (HG/SiO$_2$) efficiently promotes the cross-metathesis of methyl oleate with ethylene. Selective formation of ethenolysis products (methyl 9-decenoate and 1-decene) strongly depends on the ethylene/methyl oleate reactant ratio because the increase of $R_{C_2H_4/MO}$ ratio shifts the equilibrium to high MO conversions and suppresses the MO self-metathesis competitive reaction. However, deactivation of HG/SiO$_2$ catalysts also increases with ethylene/MO ratio. In this work, results were obtained using an initial MO/HG molar ratio of 21.2 and the ethenolysis of MO was markedly inhibited for ethylene/MO reactant ratios higher than 2.5. The highest values of yield (Y_E = 63%) and selectivity (S_E = 77%) to ethenolysis products were obtained here then at $R_{C_2H_4/MO}$ = 2.5.

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