



Short Communication

Self-metathesis of methyl oleate on silica-supported Hoveyda–Grubbs catalysts



Juan Zelin, Andrés F. Trasarti, Carlos R. Apesteguía *

Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, Santiago del Estero 2654, 3000 Santa Fe, Argentina

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ABSTRACT

The self-metathesis of methyl oleate (MO) to yield 9-octadecene and 9-octadecene-1,18-dioate (9-OD) was studied in liquid-phase on silica-supported Hoveyda–Grubbs complex catalysts (HG/SiO₂) containing 0.43–6.0 wt.% HG. The reaction was carried out in a batch reactor at 303–343 K and 101.3 kPa, using cyclohexane as solvent. HG/SiO₂ catalysts were active and highly selective for the MO metathesis reaction; equilibrium values of MO conversion and 9-OD yield were reached in 80 min. No catalyst leaching took place in cyclohexane. Catalysts containing HG >0.87 wt.% showed no significant deactivation after two consecutive catalytic tests.

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1. Introduction

Fatty acid methyl esters (FAME) are usually obtained from the transesterification of natural oils and fats with a lower alcohol. Most of oleochemical 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, ozonolysis and hydrogenation is becoming increasingly important at industrial level [1,2]. Olefin metathesis is a very powerful tool for the efficient catalytic formation of carbon–carbon double bonds allowing the synthesis of various useful intermediates and compounds for fine chemistry and for the synthesis of polymers. FAME metathesis has been studied in homogeneous catalysis using mainly Grubbs' Ru complexes [3] as recyclable catalysts. In particular, second generation ruthenium Hoveyda–Grubbs (H-G) catalysts (Fig. 1) present high activity and selectivity, and also exhibit remarkable stability to the presence of moisture and oxygen [4,5]. 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 HG catalysts for the metathesis of functionalized substrates. Other than the requirements of high activity and selectivity,

suitable solid catalysts for the metathesis of functionalized olefins should tolerate the presence of polar functional groups.

Several methods for immobilization of HG-type complexes have been studied [6–8], but frequently the resulting catalysts suffer from leaching or losses of activity as a result of immobilization. Recently, it has been reported that commercially available Ru–alkylidene complexes immobilized on SiO₂, MCM-41 and SBA supports can be employed without leaching in some solvents or significant activity loss for olefin metathesis reactions (ROMP, RCM, CM) [9–11]. Here, we study the self-metathesis of methyl oleate (MO) on Hoveyda–Grubbs complexes supported on commercial silica to yield 9-octadecene-1,18-dioate (9-OD) and 9-octadecene (Fig. 2). The synthesis of diesters such as 9-OD from the self- and cross-metathesis of FAME was one of the first reactions studied in oleochemistry [12] because unsaturated diesters are valuable intermediates for the production of polymers and fine chemicals [13,14]. The reaction of Fig. 2 has been studied on methyltrioxorhenium (CH₃ReO₃) and Re₂O₇/SiO₂–Al₂O₃ promoted with SnBu₄ [15,16] but not on HG complex supported on solid supports. Our results in the present study show that silica-supported HG complexes are stable, highly active and selective catalysts for the metathesis of methyl oleate.

2. Experimental

Five HG/SiO₂ samples containing 0.43, 0.87, 1.21, 1.67 and 6.0 wt.% HG (Sigma-Aldrich, 97%) were prepared by impregnating at 298 K a commercial silica (Sigma-Aldrich G62, 230 m²/g, 200 mesh) previously calcined 2 h at 773 K with a solution of HG in cyclohexane.

The crystalline structure of the samples was determined by X-ray diffraction (XRD) using a Shimadzu XD-D1 diffractometer and Ni-filtered

* Corresponding author at: INCAPE, Santiago del Estero 2654, 3000 Santa Fe, Argentina. Tel.: +54 342 4555279; fax: +54 342 4531068.

E-mail address: capesteg@fiq.unl.edu.ar (C.R. Apesteguía).

URL: <http://www.fiq.unl.edu.ar/gicic/> (C.R. Apesteguía).

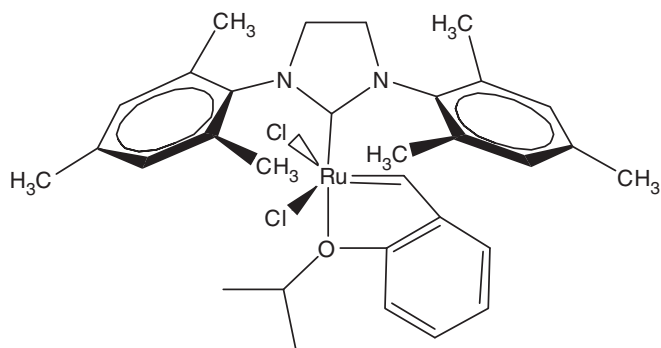


Fig. 1. Second generation ruthenium Hoveyda–Grubbs catalyst.

Cu K α radiation. The Ru content in HG/SiO₂ 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 thermal stability of HG complex was studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Shimadzu IRPrestige-21 spectrophotometer, equipped with an in-situ high-temperature/high pressure SpectraTech cell and a liquid nitrogen-cooled MCT detector. The sample holder, a ceramic crucible containing a heating resistor and a thermocouple, was placed inside a dome with CaF₂ windows. The spectral resolution was 4 cm⁻¹ and 140 scans were added. The DRIFT spectra were collected in Ar (60 ml/min). The HG(6%)/SiO₂ sample was also characterized by DRIFTS at 303 K. The spectrum of silica support was previously collected. The IR spectrum given herein for HG(6%)/SiO₂ is the difference spectrum where the SiO₂ spectrum served as the reference.

The self-metathesis of methyl oleate (Sigma-Aldrich, 99%) was carried out in a glass batch reactor under Ar atmosphere, at 101.3 kPa and temperatures between 303 and 343 K. Cyclohexane (Sigma-Aldrich, anhydrous 99.5%) previously dehydrated in a reflux distillation column was used as solvent. Variable amounts of MO and the catalyst together with cyclohexane (10 ml) and n-dodecane (internal standard) were added to the reactor and agitated with a magnetic stirrer; then the reaction mixture was heated to the reaction temperature in a thermostatic bath. Product concentrations were followed during the reaction by ex-situ gas chromatography using a Agilent 6850 GC chromatograph equipped with flame ionization detector, temperature programmer and a 50 m HP-1 capillary column (50 m \times 0.32 mm ID, 1.05 μ m film). Product identification was carried out using gas chromatography coupled with mass spectrometry (Varian Saturn 2000) both equipped with a VF5-HT capillary column. Data were collected every 10–20 min for 160–250 min. The only products detected were 9-octadecene and 9-octadecene-1,18-dioate (9-OD).

MO conversion was calculated as $X_{MO} = (C_{MO}^0 - C_{MO})/C_{MO}^0$, where C_{MO}^0 is the initial concentration of MO and C_{MO} is the concentration of

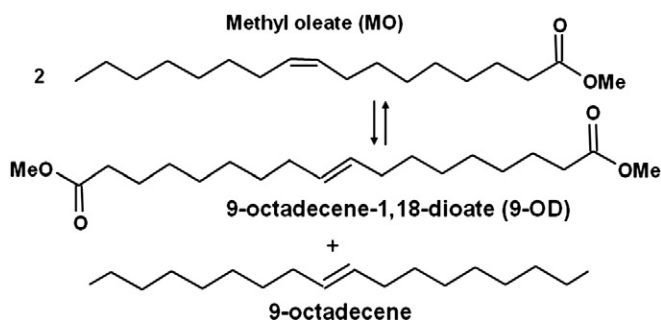


Fig. 2. Self-metathesis of methyl oleate.

MO at reaction time t . Yields (η_j , mol of product j /mol of MO fed) were calculated as $\eta_j = C_j v_{MO}/C_{MO}^0 v_j$, where v_{MO} and v_j are the stoichiometric coefficients of MO and product j , respectively. Selectivities (S_j , mol of product j /mol of MO reacted) were calculated as $S_j = \eta_j/X_{BN}$.

3. Results and discussion

3.1. Catalyst characterization

The XRD diffractograms of HG complex [17], silica support and HG(0.87%)/SiO₂ sample are shown in Fig. 3. The diffractogram of HG(0.87%)/SiO₂ presented only the amorphous halo of SiO₂ support. No diffraction peaks attributable to the HG crystalline structure were detected, probably reflecting both the low HG loading and a high dispersion of the HG complex on the support as it has been observed by other authors [9].

The thermal stability of HG complex was studied by DRIFT spectroscopy and the results are presented in Fig. 4. The IR spectrum of HG complex dried at 303 K was similar to those reported by other authors [18]. Several absorption bands appeared in the 1200–1700 cm⁻¹ region. The bands at 1651 cm⁻¹, 1454 cm⁻¹, and 1298 cm⁻¹ correspond to ν (C C) styrene, ν (C C) aromatic and δ (CH₂), respectively [18]. Typically, the intensity of the styrene vibration ν (C C) at 1651 cm⁻¹ is relatively weak in the HG spectrum due to coordination to Ru. In the 2800–3200 cm⁻¹ region the absorption bands at 2945 cm⁻¹ and 2976 cm⁻¹ are attributable to ν (CH₃, CH₂) asymmetric and ν (CH₃, CH₂) symmetric stretches. Essentially the same HG DRIFT spectrum was obtained after heating the HG complex at 373 K but further treatment at 423 K caused the disappearance of several absorption bands, probably reflecting the partial decomposition of the HG complex. The HG(6.0%)/SiO₂ sample dried at 303 K presented the main IR bands characteristics of pure HG complex, thereby indicating that the HG structure was preserved after its deposition on silica.

3.2. Self-metathesis of methyl oleate on HG/SiO₂ samples

Taking into account the results in Fig. 4 on the thermal stability of HG complex, we performed all the catalytic tests for the self-metathesis of methyl oleate at temperatures lower than 373 K. Fig. 5 shows the MO

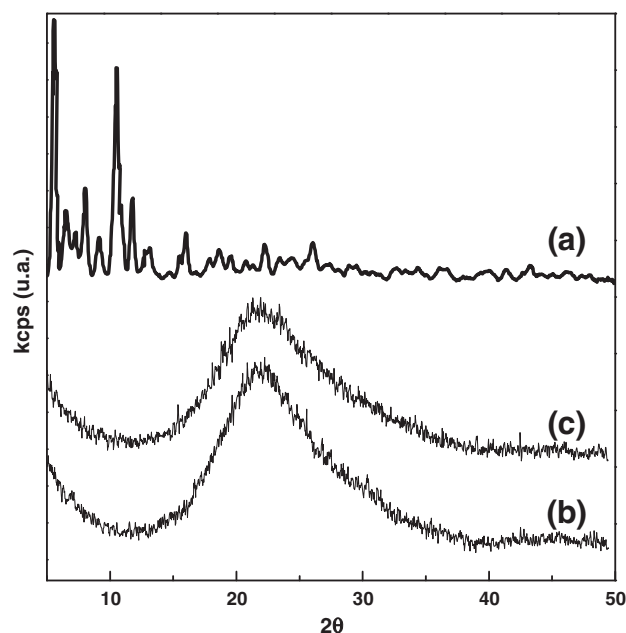


Fig. 3. XRD diffractograms of: (a) HG complex (from 17); (b) SiO₂; (c) HG(0.87%)/SiO₂.

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