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Short Communication

Ionic-tagged catalytic systems applied to the ethenolysis of methyl oleate

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ABSTRACT

A novel high selective ionophilic Hoveyda-type complex for the methyl oleate ethenolysis was prepared from Grubbs first generation catalyst. Ethenolysis under classical biphasic systems in ionic liquids showed to be mass-transference limited. This drawback was successfully solved by the catalyst dispersion on high specific surface area inorganic supports through a thin layer of ionic liquids (ILs). The supported ionic liquid phase (SILP) catalyst properties were patterned by the support type, IL cation and support/IL mass ratio. The SILP prepared with the IL 1-isopentyl-3-methylimidazole hexafluorophosphate and silica showed a turnover number higher (up to 2350) than that of biphasic systems (up to 1045).

1. Introduction

The cross-metathesis of natural derived fatty acid esters with ethylene (ethenolysis) is one of the most attractive methods for the production of high value chemical intermediates that have various industrial applications [1]. In fact, there has been an increase in academic and industrial interest in transforming internal olefins derived from seed oils to α-olefins [2,3]. In particular, there are various reports on the use of ruthenium-based Grubbs-type metathesis catalysts for the ethenolysis of the model substrate methyl oleate (Scheme 1) [4,5]. It is well established that these ruthenium complexes catalyse the ethenolysis of methyl oleate under homogeneous conditions and, in particular, Hoveyda-type catalyst precursors are highly selective for the formation of 1-decene and methyl-9-decenoate [6,7]. However, these organometallic homogeneous processes still suffer classical drawbacks, such as separation of the products from the reaction mixture, the recovery and re-use of the catalysts, and the substitution of volatile organic solvents [8].

The immobilisation of the Ru catalyst precursors on ionic liquids (ILs) is one of the most promising approaches to solve the above mentioned basic problems [8,9]. The attachment of an imidazolium moiety to either a phosphine or carbene ligand (Fig. 1) is important, not only for the immobilisation of Ru–carbene complexes in ionic liquids, but also for the stabilisation of the catalytically active species [10–13]. For example, a continuous flow self-metathesis of methyl oleate using a supported ionic liquid phase catalyst (SILP) prepared with ionic-tagged Grubbs–Hoveyda 2nd generation catalyst (**7**) in silica using CO_2 as a transport vector allows the use for at least 10 h [14]. The efficient and selective cross-metathesis of methyl oleate with ethylene can be achieved under mild conditions of catalyst **8** dissolved in *n*-1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide IL [15]. Therefore, it is possible to design a more stable, recyclable catalyst for the ethenolysis of natural derived fatty acid esters. In principle, this could be achieved through supported IL catalysts by the proper combination of the inorganic support/IL and the ionic-tagged Ru metathesis precursor.

Here, we report our preliminary efforts for obtaining catalytic systems (biphasic systems and SILP) for the ethenolysis of methyl oleate based on ruthenium catalysts containing imidazolium moieties attached to carbene derivatives.

2. Experimental

2.1. General remarks

The catalyst precursor manipulations were performed in a drybox or using standard Schlenk techniques. Ethylene Grade 2.5 (99.5%) was purchased from White Martins, standardised Alumine 90 (CAS 134428-1) was obtained from Merck, Celite 545 (CAS 68855-54-9) was from Nuclear, and Silica Aerosil 200 (CAS 7631-86-9) was from Degussa. Toluene, tetrahydrofuran, and dimethylformamide were distilled from Na/benzophenone, and CH_2Cl_2 was distilled from $CaCl_2$ and then degassed. Hoveyda catalysts **9** and **10** and Grubbs catalysts **11** and **12** (Fig. 2) were obtained from the Aldrich supplier. The ionic liquids *n*-1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($BMI \cdot NTf_2$), *n*-1-butyl-3-methylimidazolium hexafluorophosphate ($BMI \cdot PF_6$), and 1-isopentyl-3-methylimidazolium hexafluorophosphate ($iPMI \cdot PF_6$)

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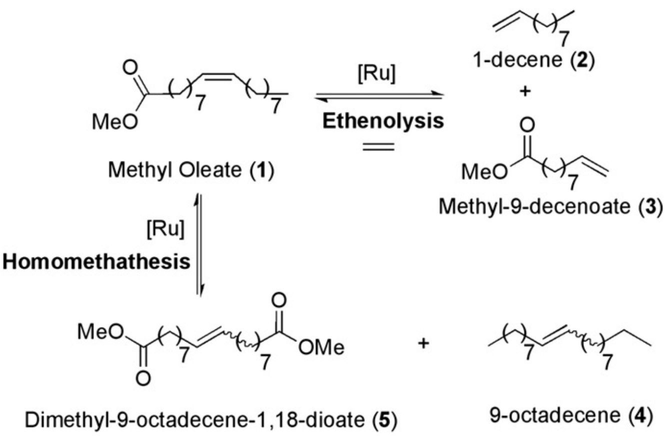

Scheme 1. Ruthenium catalysed methyl oleate metathesis.

[16] and the Ru-imidazolium-tagged carbene complexes **13** and **14** [12] (Fig. 2) were synthesised as previously reported. Other solvents and reagents were acquired from Aldrich and Acros suppliers, and used without further purification.

NMR spectra were recorded on a 400 MHz Varian spectrometer at ambient probe temperatures and referenced to internal TMS or external H_3PO_4 (see NMR spectra in Supporting information). GC analyses were performed using a Shimadzu 2010 Plus instrument equipped with a capillary column (Testek Rtx@1 — 30 m, 0.25 mm). GC–MS data were recorded on a Shimadzu QP2010 and ESI/MS on a Micromass Q-TOFmicro.

2.2. Preparation of a ruthenium-supported ionic liquid phase catalyst (Ru-SILP)

The solid supports used (alumina, celite, and silica) were exposed to a temperature of 600 °C for 2 h, cooled in a desiccator, and then maintained under vacuum for 3 h to eliminate oxygen and hydroxyl groups. The pretreated solid support, IL, catalyst precursor, and dichloromethane were added to a Schlenk and mixed vigorously for 1 min. The mixture was kept under vacuum for 30 min to completely remove the solvent. The Ru-SILP was prepared under argon using standard Schlenk tube techniques just before the reactions were conducted. The prepared Ru-SILP catalysts were identified as *SILP-Complex.Support-Weight ratio IL/Support* as shown in Table 1.

2.3. Standard substrate

Methyl oleate to a level of 95% was obtained from double distillation of MO 75% through a Vigreux column (25 cm) under vacuum. The distillate was characterised by GC, GC–MS, and ^1H NMR (see Supporting information). Peroxide was not detected by Quantofix® stick test with a detection limit of 0.5 ppm. Chromatographic internal standard (propylbenzene, 0.4393 g) was added to MO (47.8604 g), and the mixture was degassed and then maintained in a drybox for further ethenolysis reactions.

2.4. Typical procedure for catalytic tests

In a drybox, a stainless steel reactor was charged with the standard substrate (1 g, 3.2 mmol of MO) and catalyst (0.1 mol% of Ru). Next, the reactor was pressurised with ethylene (constant pressure of 20 bar) and the reaction mixture was stirred for 24 h at 30 °C. Samples were analysed by GC and the reaction products were identified by GC–MS. When biphasic system was employed the reactor was charged also with the IL (0.5 g). For reactions with supported catalysts the amount of SILP employed was based on Ru content.

3. Results and discussion

3.1. Preliminary studies

Several studies have been reported in which homogeneous ruthenium catalysts have been successfully employed in the methyl oleate ethenolysis [4–6]. However, these results often differ due to substrate purification, catalyst loading, and reaction conditions. To establish the best comparative parallel, the starting point of this work was the ethenolysis of methyl oleate with Hoveyda and Grubbs complexes (Table 2). Complex **12** showed low selectivity for ethenolysis, even when the ethylene pressure was increased from 8 to 20 bar (entries 1 and 2, Table 2), while complex **11** showed high selectivity for ethenolysis (>93%, entries 3–6, Table 2). By decreasing the ethylene pressure from 20 to 4 bar (entries 3 and 4, Table 2), a reduction in the conversion of MO was observed while maintaining the selectivity. The best ethenolysis turnover number (TON_E) was obtained with 45 ppm of complex **11** (entry 6, Table 2).

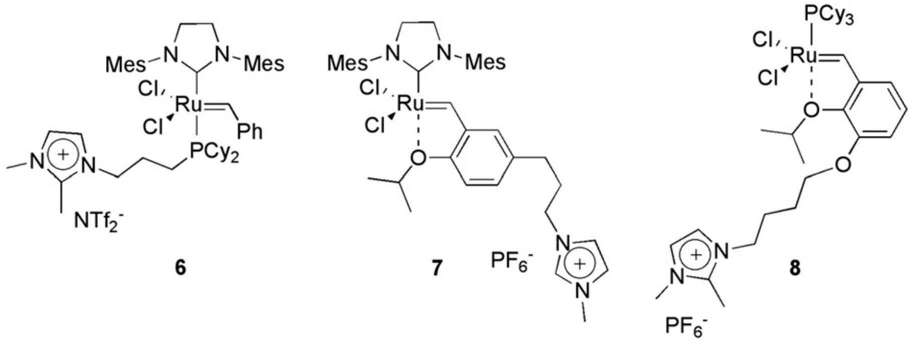

Fig. 1. Ru–imidazolium-tagged complexes.