Functionalized Olefin Metathesis in Oleochemistry: Self-metathesis of Methyl Oleate on Solid Catalysts

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Introduction

Fatty acid methyl esters (FAME) are usually obtained from the transesterification of natural oils and fats with a lower alcohol. 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 is becoming increasingly important at industrial level. In particular, 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 Ru complexes such as Hoveyda-Grubbs (HG) complexes as recyclable catalysts, but very few papers have investigated this reaction on solid catalysts. Most examples of silica-immobilized Grubbs catalysts refer to the covalent anchoring of the metal-containing moiety to preformed porous or non-porous silicas. Here, we studied the self-metathesis of methyl oleate (MO) on both Hoveyda-Grubbs complexes supported on silica and methyltrioxorhenium (MTO, CH_3ReO_3) supported on SiO_2-Al_2O_3. The MO metathesis (Figure 1) yields 9-octadecene and 9-octadecene-1,18-dioate (9-OD), a valuable product used in polymer, fragrance, lubricant, and fine chemistry industries.

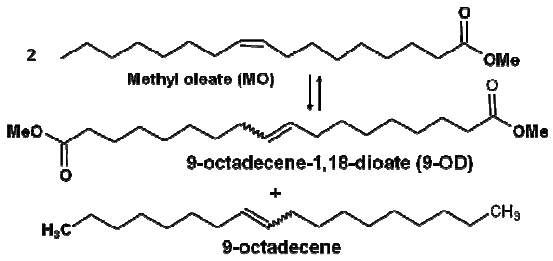


Figure 1: Self-metathesis of methyl oleate

Materials and Methods

Four HG/SiO_2 samples containing 0.43, 0.87, 1.24 and 1.61%wt HG were prepared. Solutions of HG in toluene were impregnated on commercial silica (Sigma-Aldrich G62, 250 m^2/g) at 25ºC. Solutions of MTO (1.64%) in cyclohexane were supported under inert atmosphere on Al_2O_3 and SiO_2-Al_2O_3 (12% Al_2O_3). The liquid-phase MO metathesis was carried out at 30-70ºC and 101.3 kPa in Ar, using cyclohexane as solvent. Product concentrations were followed by ex-situ gas chromatography using n-dodecane as an external standard. Data were collected every 15-20 min for 150-250 min.

Results and Discussion

Characterization by DRIFTS showed that the HG structure on HG/SiO_2 was stable up to 110ºC. The activity of HG/SiO_2 samples increased with both the %HG and the temperature. At 30ºC, the MO equilibrium conversion (50%) and the 9-OD and 9-octadene equilibrium yields (50%, molar) were reached only on HG(1.24%)/SiO_2 and HG(1.61%)/SiO_2 catalysts, being the C balance near 100% (Figure 2). For HG(0.87%)/SiO_2 and HG(0.43%)/SiO_2 the 9-OD yields were 44 and 15%, respectively. In all the cases, the HG leaching was negligible during the progress of the reaction showing the effective immobilization of the HG complex on the silica surface.

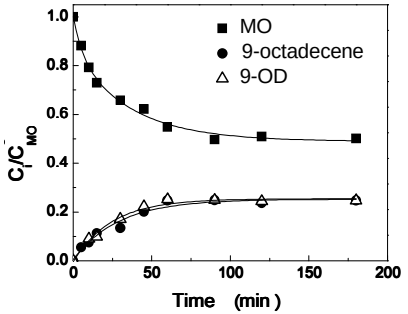
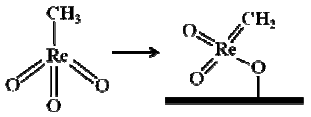


Figure 2: MO metathesis on HG(1.61%)/SiO_2

MTO is active for olefin metathesis and may also promote the metathesis of functionalized olefins, but only on the surface of solid acids [1]. Here, we observed that unsupported MTO and MTO/Al_2O_3 were inactive for MO metathesis. In contrast, MTO/SiO_2-Al_2O_3 yielded 58% of 9-octadecene at 80% MO conversion, thereby confirming that MTO became active for metathesis reactions when supported on acidic carriers. Formation of active carbene species CH_2ReO_3 would result from the C–H activation of the methyl ligand of CH_3ReO_3 onto reactive surface Lewis acid sites (Figure 3). However, the presence of 9-OD in the reaction mixture was negligible during the MO metathesis on MTO/SiO_2-Al_2O_3, probably because 9-OD remained strongly adsorbed on the support. This explains also that MO was converted beyond the equilibrium. Thus, the nature, density and strength of surface acid sites determine not only the efficient activation of the MTO complex but also the 9-OD adsorption strength formed in MO metathesis.



Inactive dissolved MTO Active carbene species

Figure 3: Formation of active supported MTO

Significance

HG/SiO_2 is an active, selective and stable catalyst for methyl oleate metathesis. Methyltrioxorhenium on acid supports is also active for this reaction but the diester formation is hampered by its strong adsorption on the support.

References

1. Oikawa, T., Masui, Y., Tanaka T., Chujo, Y., Onaka, M., Smith, J., and Smith, P., *J. Org. Chem.* 692, 554 (2007).