Synthesis of single-site Ru-NHC based heterogeneous catalysts: application to bio-resources transformation and CO₂ valorisation

C. Thieuleux[1,2], M. Baffert[1], I. Karame[1], T. Maishal[1], C. Copéret[1,2], L. Veyre[1]

[1] Université de Lyon, Institut de Chimie de Lyon, LC2P2, UMR 5265 CNRS-CPE Lyon-UCBL, CPE Lyon, 43 Bvd du 11 November 1918, 69100 Villeurbanne, France.
[2] ETH Zürich, Department of Chemistry, Wolfgang-Pauli-Str. 10, 8093 Zurich, Switzerland.
*corresponding author: thieuleux@cpe.fr

Introduction

In the context of sustainable development, efforts have to be done to produce goods, raw materials and chemicals by taking into account environmental constraints. In this context, CO₂ transformation to organics is a very promising approach because million tons of CO₂, one of the major greenhouse effect gas, are produced yearly and flared into the atmosphere. Likewise, the increase of oil prices and the decrease of the fossil resources encourage to extend the use of renewable resources to produce organic compounds. In this context, we have recently developed well-defined supported Ru-N-heterocyclic carbene (NHC) complexes onto mesostructured silica matrices as catalysts for the hydrogenation of CO₂ in presence of amines and the self-metathesis of ethyl-oleate (fatty ester from colza plants).

Materials and Methods

The catalysts preparation is described below. They were characterized by HRTEM, IR spectroscopy, N₂ adsorption/desorption and advanced solid state NMR. CO₂ hydrogenation tests were conducted using a 300mL-autoclave loaded with 3.6 µmol of catalyst and 6.0 mL pyrrolidine under an inert atmosphere. The autoclave was then pressurized at room temperature with 50 bar CO₂ and 50 bar H₂, before being heated up to 100°C. After 5 h, the apparatus was cooled down to around 50 °C and depressurized before analysing the liquid residue by GC. Self metathesis of ethyl oleate tests were carried out in a glove-box, ca. 6 mL of ethyl-oleate (16.5 mmol) were added onto 10 mg of Ru-materials (EO/Ru = 30000). Aliquots of the supernatant solution were withdrawn, quenched with ethyl acetate and filtered over a Celite pad, and the conversion (conv.) was monitored by gas chromatography using a FAME column.

Results and Discussion

In the present study, we developed, fully characterized and tested five Ru-NHC based catalysts in the self-metathesis of ethyl-oleate. The Ru-NHC supported catalysts were obtained in three steps: i) first, the preparation of platform materials containing halogenoalkyl-chains, arylimidazol-units or azido-groups by sol-gel process using a templating route, ii) the in-situ transformation of the organic functionalities into N-heterocyclic carbenes and iii) the coordination of Ru complexes on the carbene ligands. These solids exhibit similar textural (BET surface area of ca. 900 m²/g and pore diameters of 8-9 nm) and structural properties (2D hexagonal arrangement of the porous network). They all contain Grubbs II type complexes immobilized to the silica via the NHC unit and differ by the nature of the organic tether between the silica matrix and the NHC group. Among the catalysts tested, we could discriminate three groups: i) the highly active catalysts for which the Ru-NHC sites are linked to the silica surface by short flexible tethers (Fig. 1). These catalysts can reach rapidly the conversion (50%) imposed by thermodynamic equilibrium using a substrate/catalyst ratio of 30 000; ii) a medium group for which Ru-NHC are bonded to the silica matrix via long flexible or short rigid tethers (Fig. 1) and finally, iii) a poor catalyst for which the Ru-NHC site is isolated from the silica surface by a long rigid tether (fig. 1). A full characterization of these materials using advanced solid-state NMR (DPF SENS NMR) demonstrates that secondary surface interactions between the organometallic species and the silica surface is a key factor for rate and productivity.

Figure 1. Comparison of the catalysts performances

Using a similar synthetic approach, silica tethered mono NHC systems [Ru(NHC)(Cl)(PMé₃)] and dinuclear bis-NHC derivatives [Ru₂(NHC)(Cl)(PMé₃)] were developed for CO₂ hydrogenation. For mono-NHC catalysts, performances are below those obtained for the best homogeneous catalysts RuCl₃(Phosphine). This difference was attributed to the low stability of the NHC-Ru bond under the reaction conditions as shown by the important Ru leaching (50%). The bis-NHC systems display much improved activity (TON = 8780) and stability compared to the mono-NHC systems (no Ru leaching) even at 200°C.

Significance

Using an original and versatile methodology, we were able to synthetize well-defined Ru-NHC based catalysts. These catalysts were found to be highly active in CO₂ hydrogenation and self-metathesis of ethyl-oleate. Their complete characterization using advanced solid-state NMR techniques demonstrated that secondary surface interactions between the organometallic species and the silica surface was a key factor for productivity.

References