MaCaHet

New stable, well-defined and bi-functional heterogeneous catalysts highly active in the reaction of metathesis of functionalized olefins

Blanc 2008

Dr. Chloé THIEULEUX

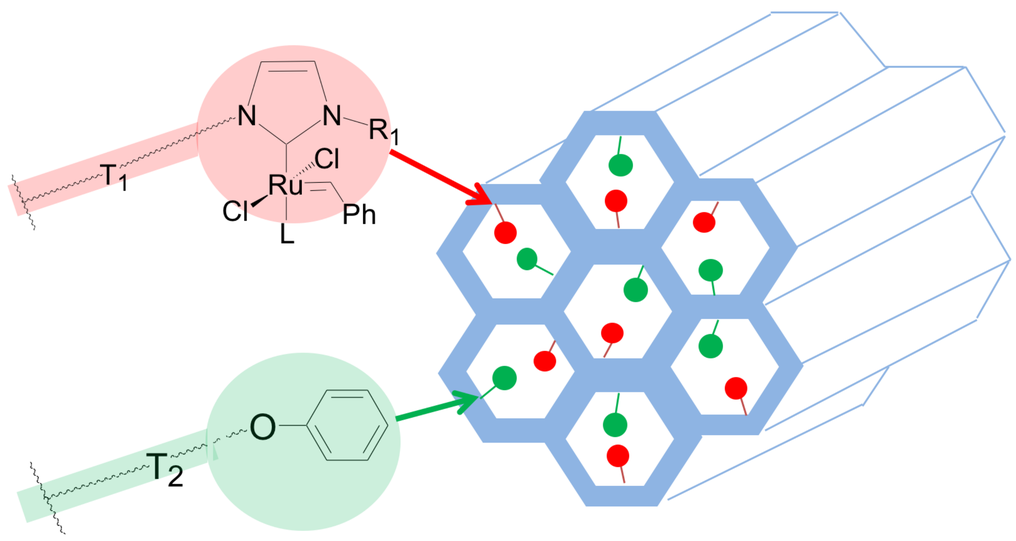
Chargée de Recherches CNRS (CNRS Researcher)

Université de Lyon, Institut de Chimie de Lyon, UMR 5265 CNRS-UCBL-ESCPE Lyon, Laboratoire de Chimie Catalyse Polymères et Procédés, Equipe COMS

Context, methodology

The catalytic reaction of functionalized olefin metathesis has become a key reaction in organic synthesis, because it is atom economical and environmentally friendly. However, it has been poorly industrialized so far because of the lack of appropriate catalysts – classical heterogeneous catalysts being poorly active and homogeneous catalysts deactivating too fast and being difficult to separate from the reaction products.
Thus, this project aims at obtaining stable and highly active well-defined heterogeneous catalysts.

Methodology.
The development of well-defined mono- or bi-functional catalytic materials containing Ru-NHC active sites was achieved by Sol-Gel process *via* the co-hydrolysis and co-condensation of an organosilane and a tetra-alkosilane precursor in the presence of a structure directing agent.
This approach allowed the successful preparation of mono-functional materials containing the desired Ru-NHC sites and bi-functional materials containing a second organic group aiming at the stabilization of the vicineous Ru-NHC units.

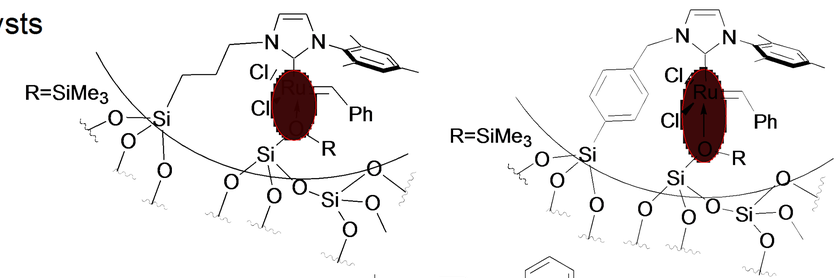


T_1, R_1= alkyle or aryle
L= PCy_3 , surface or ● T_2 = propyle or hexyle

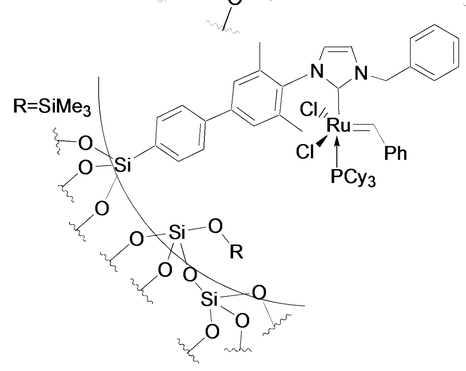
Major Results

Several catalytic mono- and bi-functional materials were prepared and fully characterized by several techniques among which Solid State NMR using Dynamic Nuclear Polarization (SENS-DNP). Their catalytic performances in several metathesis reactions were evaluated and compared to those of homogeneous counterparts and to supported catalysts obtained using grafting reactions. These studies showed the high performances, the important life-time, the recyclability of some of the catalysts and the absence of ruthenium leaching during the catalytic processes. The results also allow to determine the key parameters securing the superiority of some catalysts with respect to other ones; the key parameter being the presence of surface interactions.

Best catalysts



Worse catalysts



Perspectives and publications

These results open new perspectives for the design of heterogeneous catalysts and they led the developpement of three international collaborations and to a research contract with a important industrial group.
They also led to a european patent grant and several publications in high ranked journals :
Patent **WO2009092814; Dalton trans. 2011**, 40, 12443; **J. Am. Chem. Soc. 2010**, *132*, 15459; **J. Am. Chem. Soc. 2011**, *133*, 2104; **J. Am. Chem. Soc. 2012**, *134*, 2284

CONTACT :

Dr. Chloé thieuleux, UMR 5265,LC2P2, Equipe
thieuleux@cpe.fr
Tel: + 33 (0)4 72 43 27 95
Fax: + 33 (0)4 72 43 17 95