

Immobilized Olefin Metathesis Catalysts

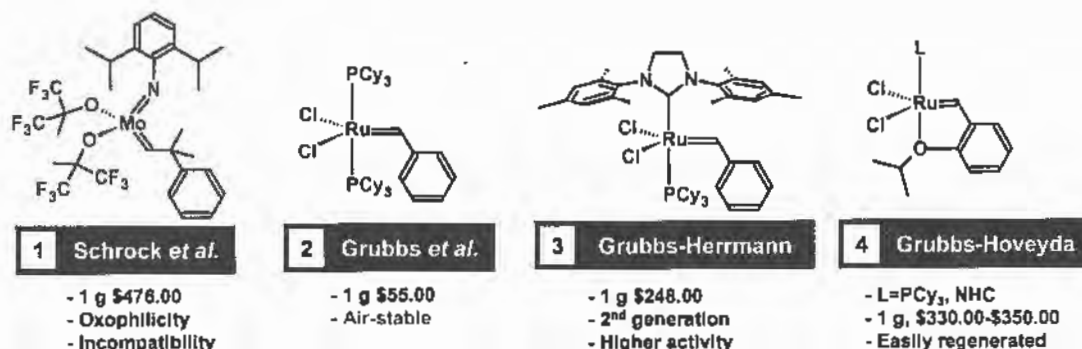
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Olefin metathesis (OM) has rapidly emerged as a powerful tool in preparation of cyclic organic compounds and polymeric materials.¹ Owing to the development and commercialization of well-defined molybdenum alkylidene catalysts by Schrock (1) and ruthenium alkylidene catalysts by Grubbs (2, 3) and Hoveyda (4), olefin metathesis reactions are now commonly used in scientific laboratories all around the world.

OM can be categorized into five major reactions. Ring closing metathesis (RCM), acyclic diene metathesis polymerization (ADMET), ring opening metathesis polymerization (ROMP), ring opening metathesis (ROM), and cross metathesis (CM). The practicality and versatility to form C-C bonds through the above mentioned reactions catalyzed by the Schrock and Grubbs catalysts increased the demand to develop easy to recyclable, more efficient, more cost-effective, and more environmental friendly catalyst systems. The use of these catalysts in variety of fields from medicinal chemistry to materials chemistry has also increased the need to get better catalyst systems.



Few purification techniques to remove the residual metal in the product have been developed by several groups. Maynard and Grubbs^{2a} used a water-soluble coordinating phosphine, tris(hydroxymethyl)phosphine, P(CH₂OH)₃, Paquette and co-workers^{2b} used lead tetraacetate, Pb(OAc)₄, Georg and co-workers^{2c} used triphenylphosphine oxide and/or dimethyl sulfoxide, and Cho and Kim^{2d} used combinations of activated carbon adsorption and simple silica gel filtration/chromatography methods. Overall, the metal content of over 70 µg/5 mg in a crude product was reduced many folds down to the range of 0.3-1.5 µg/5 mg.

Still these techniques involve toxic materials and tedious purification methods. In this regard, many heterogeneous olefin metathesis catalysts have been reported. Schrock and Grubbs type catalysts 1 - 4 were immobilized onto either polymers or inorganic solid supports. In immobilizing Grubbs type catalysts the anchor groups were carefully attached to either the alkylidene moiety, the phosphine, or the N-heterocyclic carbene

(NHC). Also halide exchange method was used. In preparing supported Mo catalysts the immobilization occurred via the alkoxide/phenoxide ligands.

First, looking at the polymer supports, in 1995 Grubbs and Nguyen reported the first immobilized well-defined Ru alkylidene catalyst.³ Earlier examples focused on using commercially available polystyrenes (PS) and depending on the system, recycling was possible but activity of the reaction was not better than the homogeneous versions.⁴ Other systems have been developed since then using polyethyleneglycol (PEG) chains and various other PS resins. Interestingly immobilization usually involved anchoring via the *i*-Pr, styrene, phosphine and NHC moiety.⁵⁻⁷

Instead of using commercially available polymer supports, research groups have recently developed systems that involve the use of radical polymerization or ROMP methodology.⁸ These catalyst had quite high TON and TOF then before. Schrock and co-workers reported the first polymer-supported and recyclable chiral Mo catalyst for enantioselective OM reactions.⁹ Their approach involved free radical polymerization. Excellent e.e.'s were achieved and recycling was easily done by filtration. Moreover metal leaching was clearly minimized (91% to only 5%) by the faint yellow product color. One step further, Buchmeiser and co-workers (Figure 1.a) recently reported another example of using ROMP methodology to generate an immobilized chiral Mo catalyst.¹⁰

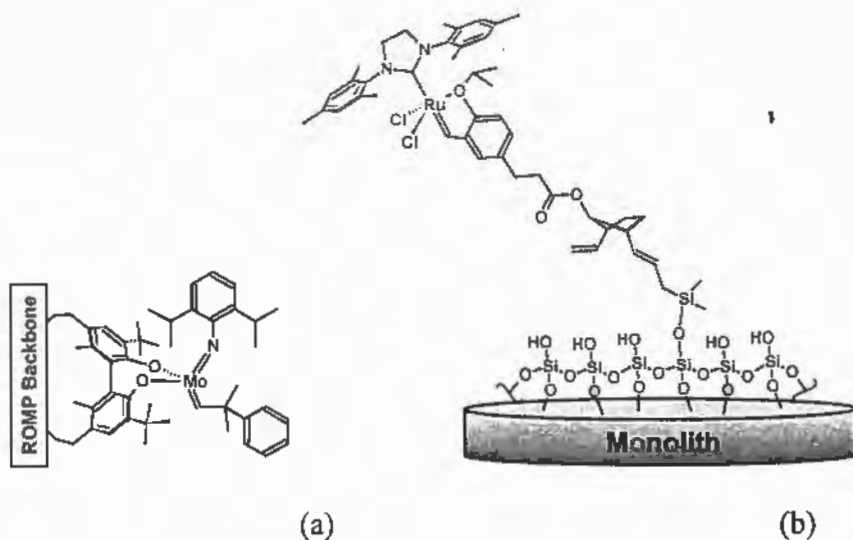


Figure 1. Immobilized Olefin Metathesis Catalysts (a) ROMP¹⁰ (b) Sol-gel monolith¹².

In the case of inorganic solid supports, several groups have reported moderate to good results. Verpoort and co-workers reported the immobilization of Grubbs catalyst 1 onto a mesoporous solid support, MCM-41.¹¹ Hoveyda and co-workers immobilized type 4 catalysts onto a monolithic sol-gel glass (Figure 1.b) which has an average pore size of 20 nm.¹² For RCM, the catalyst was reusable up to 15 cycles under inert atmosphere but under ambient conditions no reaction occurs after the 3rd cycle. Product removal is simply done by pipeting out solvents. Buchmeiser and co-workers combined the halogen exchange methodology with ROMP methodology and synthesized monolith- and silica-

based heterogeneous 2nd generation Grubbs type (3) catalysts.¹³ Accelerated initiation and increased catalyst stability were observed for the ROMP-monolith case and Ru leaching was low.

Immobilizing well-defined olefin metathesis catalysts onto polymers and inorganic solid supports, in most cases, had lower activity compared to the homogeneous cases. Metal leaching was substantially lower but recycling ability varied from system to system. Only ROMP based and monolith type catalyst systems look promising. Thus, reactivity and recycling still remains to be improved. Through the better understanding of the reaction mechanism and the relationship between catalyst, support and substrate there should be better examples to come in the future.

References

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