

Strategies towards non-covalent immobilisation of olefine metathesis catalysts

Andreas Kirschning,^{a*} Klaas Mennecke,^a Anna Michrowska^b and Karol Grela^{a,b}

^a Institut für Organische Chemie der Universität Hannover, Hannover, Germany

^b Institute of Organic Chemistry, Polish Academy of Science, Warsaw, Poland



A Introduction

During the last decade solid supports in solution phase synthesis have become a widely used tool in organic chemistry. In this context the mode of immobilization of either the reagent or the catalyst is an important aspect. Ideally the species should not be covalently attached.¹ In order to reuse and regenerate any homogenous immobilized catalyst and to apply them under continuous flow conditions ionic or coordinative strategies are favoured. In the current study, we disclose the development of a new Hoveyda-type catalyst **2** which can be immobilized as active catalyst **3** to a specially designed cationic exchange resin.

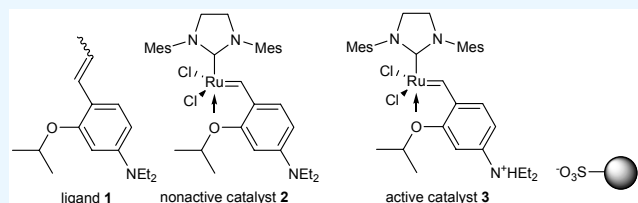


Figure 1: Precursor ligand **1**, Hoveyda-type soluble catalyst **2** and active catalyst **3**

B Ionic Immobilization of catalyst **2** to different cationic exchange resins

Catalyst **2** bearing the electron-donating NEt_2 -group shows no or very little activity in olefine metathesis reactions.² During the immobilisation of **2** the Et_2N group plays a twofold role: It is a selective anchor for the immobilisation to a cationic exchange resin and simultaneously it changes from an electron-donating- to an electron-withdrawing-group. After protonation the electron-withdrawing-group activates the catalyst by weakening the $\text{O} \rightarrow \text{Ru}$ chelation and then facilitates faster initiation of the catalytic cycle.³

After evaluation of different cationic exchange resins we choose to take Dowex®50Wx2 and a sulfonated polystyrene which was synthesized by precipitation polymerization. The selfmade polymer was prepared from a heated solution (70°C) of the monomers styrene and divinylbenzene and AIBN as radical initiator in a nonpolar solvent (n-alkane C14-C17 mixture). After 12 h the precipitation of small interconnected polymer particles was observed. The following sulfonation was achieved by treatment of the filtered and washed polymeric particles with a solution of chlorosulfonic acid for one day to yield an acidic ion exchange resin (4.5 mmol/g capacity; 5.3 mass% degree of crosslinking).

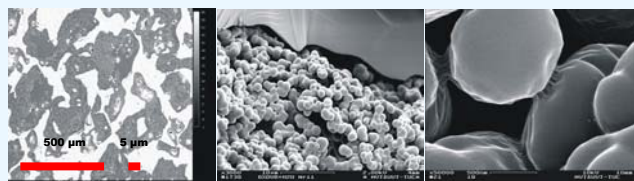


Figure 2: Scanning electron image of the polymer

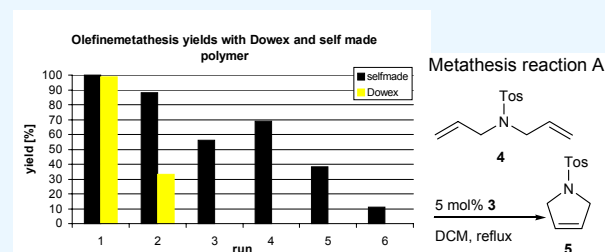


Figure 3: Comparison of reusability between self-made and Dowex®50Wx2 loaded with catalyst **3**

From figure 3 one can clearly conclude that the polymer generated by precipitation polymerisation guaranties enhanced activity compared to the same catalyst bound to the commercial cationic exchange resin and importantly it can be reused more oftenly.

The next step was first to immobilize catalyst **2** followed by addition of the ligand **1**: The idea of this immobilization strategy is to provide more active sites in order to catch the catalyst from solution after the metathesis reaction, to minimize catalyst leaching and to increase its stability. However this protocol afforded the ring closing products in lower yield compared to the immobilization strategy described above.

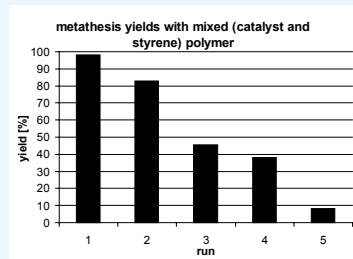


Figure 4: Yield of **5** with dual catalyst and ligand immobilisation for different runs

C Coordinative immobilization of Ruthenium-catalyst to Polyvinylpyridin

An alternative and new type of immobilization for olefine metathesis-catalysts utilizes coordinative binding. Attachment of Grubbs-III-catalyst **6** to polyvinyl pyridine (PVP) yielded polymer **7**.

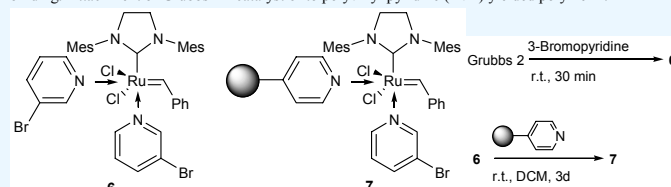


Figure 5: Grubbs-3rd-generation-catalyst and coordinative binding to PVP

The polymer resin has a capacity of 4.85 mmol/g and crosslinking was determined to be 5.3 mass% and was prepared under the same conditions described for the acidic ion exchange resin. The stability of polymer **7** was tested in model reaction B.

It can be seen that the stability of polymer **7** is slightly decreased compared to polymer **3**.

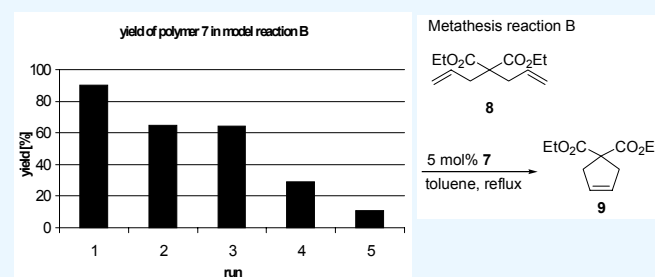


Figure 6: Stability of polymer **7** in model reaction

D Comparison of the activity of polymer **3** and **7**

A comparison of the activity of polymer **3** and **7** shows that both are active in RCM, CM and en-yne-metathesis reactions. Both catalysts show nearly the same activity except to diethyl 3-methylcyclopent-3-en-1,3-en-1,1-dicarboxylate with a 1,1-disubstituted olefinic double bond. Here catalyst **3** shows enhanced activity.

Table 1: Yields of metathesis-reactions with polymer **3** and **7** with different substrates

| substrate | Yields with polymer 3 | Yields with polymer 7 |
|---|------------------------------|------------------------------|
| | 51% | 85% |
| | 17% | 12% |
| $(\text{Ph})_2\text{Si}(\text{CH}_2\text{CHCH}_2)_2$ | 85% | 100% |
| | 100% | n.d. |
| $\text{Ph}(\text{SO}_2\text{CH}(\text{CCH}_2\text{CH}_2)_2$ | 100% | n.d. |
| | 79% | 24% |
| $\text{Tos} = \text{N}(\text{CH}_2\text{CHCH}_2)_2$ | 100% | 100% |

E Conclusion

We showed that it is possible to reversably bind Hoveyda-type catalyst **2** and Grubbs catalyst (3rd-generation) to a specially designed polymer resin. The immobilized catalysts show good stability and activity in metathesis reactions. Improvements on this new concept of immobilisation are currently und way in our laboratories

References

- W. Solodenko, T. Frenzel, A. Kirschning, in *Polymeric Materials in Organic Synthesis and Catalysis*, (Ed.: M. R. Buchmeiser), Wiley-VCH **2003** pp 201-240;
- For water-soluble Grubbs ruthenium alkylidenes bearing quaternary ammonium salts, see: D. M. Lynn, B. Mohr, R. H. Grubbs, L. M. Henling, M. W. Day *J. Am. Chem. Soc.* **2000**, *122*, 6601-6609
- K. Grela, S. Harutyunyan, A. Michrowska, *Angew. Chem. Int. Ed.*, **2002**, *41*, 4038-4040 (*Angew. Chem.* **2002**, *114*, 4210-4212)
- J.A. Love, J.P. Morgan, T.M. Truka, R.H. Grubbs, *Angew. Chem. Int. Ed.*, **2002**, *41*, 4035