PhD. Thesis

SELECTIVE HYDROGENATIONS ON ANCHORED METAL COMPLEXES

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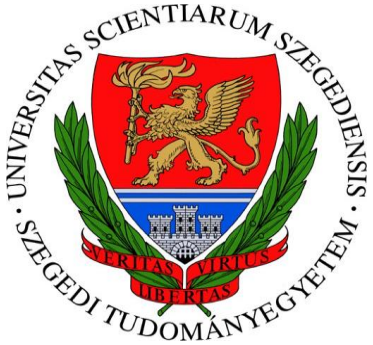

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I. INTRODUCTION

Selectivity of the catalytic processes has become an issue of increasing importance, because the production of the least amount of side products is very important for the industry, from both the environmental and economical points of view.

The academic research in organometallic chemistry has grown in the last decades and has provided much of the understanding for homogeneous catalysis. Due to this intensive research work, the steps of the homogeneous catalytic processes are well known even at a molecular level. Chemical engineers charged with applying this knowledge in the technology. In addition to, the homogeneous catalysts have identical catalytic sites and therefore usually have high selectivity.

However, the most widely used industrial catalysts are solid materials, especially metals or metal oxides, sometimes used in combination with each other, like the metals supported on metal oxides. These heterogeneous catalysts are preferred for industrial processes because they can be easily separated and reused in a subsequent cycle. Unfortunately, the surfaces of the heterogeneous catalysts are complex, and may have regions with different compositions and structures. These structures are difficult to characterize, especially under the conditions of the catalytic reactions. Because of this surface complexity, the heterogeneous catalysts have lower selectivity and their surface structures are only poorly understood in comparison with homogeneous catalysis.

Consequently, heterogenizing homogeneous complexes by immobilization is a trend toward to develop chemically homogeneous but physically heterogeneous catalysts, which can successfully combine the high selectivity of homogeneous catalysts with the easy separation and recycling of the heterogeneous ones.

The immobilization of metal complexes can be performed in two different ways. The first is the building of the metal complex inside a porous support (encapsulation), while the second is the direct attachment of the metal complex to the surface of a support by a linkage group (covalent grafting). Both of these fundamental ways of heterogenization have its own advantages and disadvantages.

The encapsulated complexes may retain their solution-like activity and selectivity, but

the diameter of the supercages determines the greatest size of the complexes can be encapsulated.

Grafting the metal complexes to a surface by covalent bonds is free from these restrictions but has often lead to unsatisfactory results, because the weak bonds can cause the leaching of the complexes, while the too strong bonds make the complexes to be rigid and it is often lead to the decrease of the selectivity. Another important drawback of the heterogenization method via covalent bonds between the metal complex and the surface of the support is the fact that the ligands have to be functionalized, which very often requires significant preparative efforts. Augustine and coworkers have introduced, however, a new immobilization procedure which can heterogenize the commercially available metal complexes without any additional structural changes.

The method involves the attachment of a metal complex to a solid support using a heteropoly acid as anchoring agent. The concept is claimed to be generally applicable for a variety of systems: montmorillonite, carbon, alumina and lanthana were used as supports, while different heteropoly acids were applied as anchoring agents. Basic alumina was found to be the best support and tungstophosporic acid was the best anchoring material.

The basic goal of my PhD work was to develop selective heterogeneous catalysts and to study the application of them. For this purposes I have prepared several metal complexes and their heterogenized analogues. The heterogenized complexes were characterized by spectroscopic methods and were applied in the selective hydrogenation of different starting materials.

II. EXPERIMENTAL METHODS

The anchored catalysts were prepared using two different methods. At the beginning of my work first preformed crystalline [Rh(nbd)(*S*,*S*)-bdpp]PF_6 type catalysts were anchored on the HPA/Al_2O_3 system.

Later the so called *is situ* anchoring method was developed. During this process the complexes to be anchored were prepared in the reaction vessel from $[Rh(nbd)Cl]_2$ and the chiral ligands, instead of using preformed ones. According to the spectropcopic data and the catalytic measurements both methods produced the same heterogenized catalysts, but the *in situ* method is much faster and cheaper. The transfer of the *in situ* prepared complexes from the flask to the other round bottomed flask containing the HPA/Al_2O_3 suspension needs air-free conditions. A simple experimental set up was developed for this purposes, in which the complex solution is transferred by argon pressure from the complex containing reaction vessel to an other flask containing the HPA/Al_2O_3 through a narrow tube connecting to the dropping funnel through a rubber cork.

The enantioselective hydrogenations of (*Z*)-2-acetamidocinnamic acid and (*Z*)-methyl-acetamidocinnamate and acetophenone derivatives were studied using the above catalysts.

New water soluble Ru(NHC) complex was prepared and immobilized by "in situ" anchoring method. The selective hydrogenation of different starting material was studied on these catalysts in organic solvent and in aqueous solution, as well.

The metal content of the anchored catalysts was determined using a JOBIN YVON 24 type ICP-AES instrument.

The FT-IR spectra of the support, the free complexes and the heterogenized samples were recorded on a Bio-Rad FTS–65 A spectrophotometer, in the range of 400 – 4000 cm^{-1}, in KBr pellets.

The solid state ^{31}P NMR spectra were recorded at room temperature using a Bruker Avance spectrometer operating at 11.7 Tesla magnetic field.

Hydrogenation experiments were done in a batch reactor of 30 mL capacity, at different temperatures and different hydrogen pressures. The reactor can be evacuated and pressur-

ized by argon or hydrogen and it is equipped with a septum for the injection of starting materials and to take samples. The reactor was shaken in a vortex manner.

Samples were taken every 10 minutes from the reaction mixture, and the products were analyzed by capillary gas chromatography. The enantiomeric excess was determined on Permabond®-CHIRASIL-L-VAL column.

III. NEW SCIENTIFIC RESULTS

1. Preformed crystalline [Rh(*S*,*S*)-bdpp]PF_6 type complexes were immobilized on Al_2O_3 support, via an anchoring method using heteropoly acid as anchoring agent developed by Augustine. Spectroscopic data showed that the homogeneous and the heterogenized complexes have similar structures and similar catalytic properties.

2. The original method was modified using *in situ* prepared complexes instead of the preformed ones. According to the spectroscopic data and the catalytic measurements both methods produced the same heterogenized catalysts, but the *in situ* method is much faster and cheaper. The immobilized catalysts produced via the *in situ* method can also be reused in several subsequent experiments without any significant loss of catalytic properties.

3. The *in situ* prepared heterogenized catalysts were successfully applied in the hydrogenation of (Z)-2-acetamidocinnamic acid. The specific activity of the immobilized samples were higher than the activity of the homogeneous analogs, in a good correlation with our former findings.

4. The differently substituted immobilized [Rh(*S*,*S*)-bdpp] complexes showed electronic tuning similar to the homogeneous complexes, namely the activity increased with the ligand basicity. The same was true for the enantioselectivity, too, but the extent of the effect was much lower.

5. The hydrogenation rate of the (*Z*)-methyl(2-acetamidocinnamate) was lower than that of the acid, but otherwise the ester hydrogenation was similar to the hydrogenation of the acid.

6. The *in situ* prepared anchored Rh complexes were also used for the enantioselective hydrogenation of the C=O bonds of acetophenone derivatives. Using the conditions developed for the homogeneous complexes to hydrogenate the C=O bond, the anchored catalysts were

also able to hydrogenate the C=O bonds with reasonable activity and enantioselectivity.

7. The heterogenized complexes were slightly less reactive than the homogeneous ones. This observation is in contrast to our earlier results, since so far we usually had higher activity on the heterogenized samples.

8. Considering the differently substituted acetophenone derivatives the heterogenized catalysts show the similar substituent effect as the homogeneous complexes but this effect not so explicit than in the case of soluble complexes.

9. The Sheldon test also confirmed the absence of the leaching which was concluded formerly from the unchanged activity of the recycling experiments.

10. A new, heterogenized Ru(II)-*N*-heterocyclic carbene complex was prepared on Al_2O_3 via the anchoring method developed by Augustine. The immobilized complex had a reasonable activity in the hydrogenation of C=C and C=O bonds in both ethanol and water. At the same time it was possible to filter out the anchored catalysts from the reaction mixture and to recycle in several subsequent runs without any significant loss of catalytic properties.

11. The specific activities of the heterogenized complexes in this case were usually lower than those of the homogeneous ones.

12. During the hydrogenation of *trans*-cinnamaldehyde the chemoselectivity was shifted from the preferential C=C hydrogenation to the hydrogenation of both groups and the C=C and C=O bonds were hydrogenated almost to equal extent.

13. In the presence of triphenylphosphine neither acetone nor acetophenone could be hydrogenated. Conversely, propanal, *trans*-cinnamaldehyde and allyl alcohol were hydrogenated with good conversions. Using triphenylphosphine in the case of *trans*-cinnamaldehyde, selective C=O hydrogenation occurred. It seems likely that PPh_3 replaces one of the Cl^- ligands in $[RuCl_2L(C_{10}H_{14})]$, resulting in the formation of a new catalytic species.

14. In the case of allyl alcohol a fast C=C hydrogenation occurred, and propan-1-ol

was produced and isomerization to propanal was observed.

15. One of our goal was to check the applicability of the anchored complexes in water, with special regard to the use of heteropoly acid as anchoring agent. To our knowledge this was the first example of applying a heterogenized *N*-heterocyclic carbene complex catalyst in aqueous medium.

16. It can be concluded, that the heterogenized catalysts, prepared by the method of Augustine, are suitable for the use in aqueous reaction media, too, furthermore specific activities were found considerably higher in aqueous systems than in ethanol as solvent.

IV. PUBLICATIONS

1. Journal articles

1. Substituent effects in enantioselective hydrogenations catalyzed by immobilized Rh complexes
Á. Zsigmond, **S. Undrala**, F. Notheisz, A. Szöllősy, J. Bakos
Applied Catalysis A: General, 303 (2006) 29-34
Impact factor: 2.825

2. New application of an anchored Ru(II)-*N*-heterocyclic carbene complex
Á. Zsigmond, **S. Undrala**, F. Notheisz, G. Papp, F.Joó
Catal. Lett., 105 (2007) 163-168
Impact factor: 1.904

3. The effect of substituents of immobilized Rh complexes on the asymmetric hydrogenation of acetophenone derivatives
Á. Zsigmond**, S. Undrala** , F. Notheisz, Á. Szőllősy, J. Bakos
Centr. Eur. J. Chem., 6 (2008) 549
Impact factor: 0.754

∑ **i = 5.48**

2. Scientific lectures

1. Szubsztituenshatás vizsgálata a Rh-katalizált aszimmetrikus hidrogénezésekben
Á. Zsigmond, U. Sushen, F.Notheisz, J. Bakos
MKE Vegyészkonferencia, Hajdúszoboszló, 2005
Előadásösszefoglalók, 21. o.

2. A simple, efficient method for heterogenization of metal complexes

Á. Zsigmond, S. Undrala, F. Notheisz, J. Bakos

XVI. FECHEM Conference on Organometallic Chemistry, Budapest, 2005 Book of Abstracts, p. 151

3. Asymmetric C=O hydrogenation on heterogenized Rh complexes

S. Undrala, F. Notheisz, J. Bakos, Á. Zsigmond

8th Pannonian International Catalysis Symposium, Szeged, 2006, Proceedings, p. 291

4. Selective hydrogenations on anchored metal complexes

S. Undrala, Á. Zsigmond

XXVIII. Kémiai Előadói Napok, Szeged, 2006

5. Fine tuning of activity and selectivity of immobilized Rh complexes in asymmetric hydrogenations

S. Undrala, F. Notheisz, J. Bakos, Á. Zsigmond

Centenáriumi vegyészkonferencia, Sopron, 2007, Előadásösszefoglalók, 384 o

6. Enantio- and chemoselective hydrogenations on heterogenized metal complexes

S. Undrala

MTA Katalízis Munkabizottsági Ülés, Budapest, 2007