Closing report

The finished research project, named *Advanced Metallo-organic Complexes for Catalysis*, was a continuation of the previous ICPF-UNI SZEGED cooperation during the period 2008-2009, within the project MEB 040802 *Advanced Catalytic Reactions for Fine Chemicals / Tervezhető katalitikus reakciók finomvegyszerek előállítására*, which was believed to be very successful in many aspects (also reported in the AIP Bulletin 2010). The publication and other outputs of the previous cooperation, including the paper in a journal with high Impact Factor (4.8), and a common book chapter (Springer Verlag). This newly finished project was addressed the very up-to-date topic: utilization of homogeneous metallo-organic complexes in advanced catalytic processes, with a special focus on oxidations and hydrogenations. Homogeneous catalysts, very often based on utilization of metallo-organics, are mixed with the reactants at the molecular level. Thus they typically show much higher activity and selectivity as they offer chemically well-defined active sites and are not limited by heat and mass transport. In practice, however, solid or immobilized homogeneous catalysts are preferred. From this reason this finished project was also addressed the topic of effective surface immobilization of particular catalytically active metallo-organics.

Our research plan **for the first year** was the following:

2012 - We were planning the preparation of a new generation of metallo-porphyrines and the study of the application of these complexes in different oxidation reactions. We wanted to extend our examination to the application of different metal-phthalocyanines, supplied by VUOS Pardubice, a traditional industrial co-operator of the Czech team.

The executed research activity partly followed our original plan, since we have applied Fe(phthalocyanine) but the reactions have changed to the catalytic transfer-hydrogenation of carbonyl functionality.

According to our original plan we have prepared different phthalocyanines – such as Zn(Pc), Al(Pc), Si(Pc), Fe(Pc), Co(Pc), Ni(Pc), Cu(Pc) - by microwave irradiation. We have also carried out some chemical modifications, in order to increase the solubility of (Pc)s in polar and non-polar solvents. The most frequent chemical modifications are the preparation of sulphonated or carboxylated derivatives. Our usually applied method was the sulphonation.

Most of the (Pc)s produces highly active oxygen either in the form of singlet $^1O_2$ or in the form of superoxide radical. Singlet $^1O_2$ is usually considered, as active species in a majority of photo-induced reactions with (Pc)s, as photocatalysts. It must be noted that (Pc)s with a completely occupied valence sphere or d-orbitals are effective photocatalysts, like Zn(Pc), Al(Pc), Si(Pc),. On the other hand (Pc)s containing metal ions with not fully occupied d-orbitals (e.g. Co^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}) tend toward rapid extinction of their excited triple states with consequences in a lower number of formed active species. These latter (Pc)s are also active in oxidation reaction, but using oxidants such as H_2O_2, or *t*-BuOOH.

During our study toward oxidation reactions we have investigated both directions: the photocatalysis and the oxidation in dark, with oxidants.

The photocatalytically active (Pc) molecules are able to absorb photons in two distinctive, well-separated regions. The major absorbance band, which is associated with the visible colour properties of (Pc)s, is located inside of the interval 500–700 nm. Significant light absorption below 400 nm comes from the interactions with highly energetic photons in the UV region.. The bimodal absorption bands in both regions is a characteristic feature revealed by all chemically modified (Pc)s due to their aggregation tendency. Besides monomers mostly dimeric forms appear and their absorption bands are those shifted toward energetically more abundant region. For the modified (Pc)s it was observed that the higher the content of more sulphonated individual derivatives, the higher was the tendency for their aggregation. On the other hand, mixtures of derivatives of (Pc)s at different sulphonation stages were not seriously affected by this phenomenon and mostly dimers appeared along with the monomeric forms.

According to our original plan we have prepared different phthalocyanines – such as Zn(Pc), Al(Pc), Si(Pc), Fe(Pc), Co(Pc), Ni(Pc), Cu(Pc) - by microwave irradiation. We have also carried out some chemical modifications, in order to increase the solubility of (Pc)s in polar and non-polar solvents. The most frequent chemical modifications are the preparation of sulphonated or carboxylated derivatives. Our usually applied method is the sulphonation.

Most of the (Pc)s produces highly active oxygen either in the form of singlet $^1O_2$ or in the form of superoxide radical. Singlet $^1O_2$ is usually considered, as active species in a majority of photo-induced reactions with (Pc)s, as photocatalysts. The active singlet oxygen form occurs when porphyrine with longer life-time of the excited triple state is involved. It must be noted that (Pc)s with a completely occupied valence sphere or d-orbitals are such structures, like Zn(Pc), Al(Pc), Si(Pc),. On the other hand (Pc)s containing metal ions with not fully occupied d-orbitals (e.g. Co^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+}) tend toward rapid extinction of their excited triple states with consequences in a lower number of formed active species. These latter (Pc)s are also active in oxidation reaction, but using oxidants such as H_2O_2, or *t*-BuOOH.

During our study toward oxidation reactions we have investigated both directions: the photocatalysis and the oxidation in dark, with oxidants.

The photocatalytically active (Pc) molecules are able to absorb photons in two distinctive, well-separated regions. The major absorbance band, which is associated with the visible colour properties of (Pc)s, is located inside of the interval 500–700 nm. Significant light absorption below 400 nm comes from the interactions with highly energetic photons in the UV region.. The bimodal absorption bands in both regions is a characteristic feature revealed by all chemically modified (Pc)s due to their aggregation tendency. Besides monomers mostly dimeric forms appear and their absorption bands are those shifted toward energetically more abundant region. For the modified (Pc)s it was observed that the higher the content of more sulphonated individual derivatives, the higher was the tendency for their aggregation. On the

other hand, mixtures of derivatives of (Pc)s at different sulphonation stages were not seriously affected by this phenomenon and mostly dimers appeared along with the monomeric forms.

2013 – Our research plan for this year was the following: The prepared metal-phthalocyanines would be immobilized in several different ways and we are going to characterize of these heterogenized catalysts. The application of these metal-phthalocyanines would be study in the oxidative degradation of different biopolimers.

In this year we followed our original research plan, we have prepared and immobilized the iron-phthalocyanine complex. The prepared catalyst was applied in the catalytic transfer-hydrogenation of of carbonyl funtionality. The iron complexes are usually applied in oxidation reactions, their applicability in reductions has been rather neglected in the past. We also wished to examine the possibility of replacing the rare transition metal catalysts with the Fe phthalocyanine complex in this reaction.

(Fe(Pc)) was prepared in the solvent free method, applying microwave irradiation. The obtained complex was characterized by FT-IR spectroscopy and the spectra revealed characteristic bands for (Pc).

In order to determine the complex concentration of the immobilized catalyst the samples were dissolved in cc. HNO_3 and the metal content evaluated. The anchored catalyst was identified to contain about 35.8 μmol of Fe /g.

To check the ability of Fe(Pc) to catalyse the CTH reactions various aldehydes and ketones with different chemical environment for the C=O functional group were used. We have done optimization experiments considering the type and amount of base, the amount of catalyst, the reaction temperature and time. After getting the optimum conditions a series of various C=O compounds, differently substituted benzaldehydes were employed in the CTH reaction. Each starting material give the suitable alcohol with reasonable conversion.

It is well known that practical catalytic processes prefer the heterogeneous catalysts over the homogeneous ones. With this in mind the heterogenized version of Fe(Pc) complex was also applied for the CTH reaction of 7 differently substituted benzaldehydes.

In heterogeneous condition we have to optimize the reaction first and the optimum condition was applied for all aldehydes. Our results clearly show that all the studied aldehydes were reduced to the corresponding alcohols with good to excellent yields. In other words the immobilized Fe(Pc) complex was proven to be a good catalyst for CTH reaction of different aldehydes.The most important advantages of the immobilized complexes are the easy separation and the possibility to recycle them.

Having obtained reasonable results for the Fe(Pc) catalysed CTH reactions of aldehydes we extended our study to the reaction of ketones. The same protocoll was followed more or less than in the case of the aldehydes and the results were similar, as well.

The most important advantage of immobilized complexes is their recyclability, which is a crucial point if the complex is expensive or difficult to get it. Iron(pthtalocyanine) is not expensive and readily available compound, however we have investigated the reusability of the heterogenized catalyst in reduction of aldehydes and ketones, as well.

Our data showed that the Fe complex is a good catalyst for catalytic transfer-hydrogenation of aldehydes and ketones, can replace the more expensive rare transition metals. We also have evidence for the recyclability of the heterogenized complex.

In the second year of our research activity year we have extended the research in an other direction, too since Dr. Ágnes Mastalir join to our group. The new direction of investigation was the investigation of a new complex on a new support: namely, the Pd(II) complex with chloride and tridecylamine ligands ($PdCl_2(TDA)_2$) was immobilized on graphite oxide modified with the cationic surfactant octadecyltrimethylammonium bromide ($C_{18}TABr$). Samples with different Pd loadings were synthesized and investigated as catalysts for the liquid-phase hydrogenation of 1-pentyne and the Heck coupling reactions of styrene-bromobenzene and styrene-iodobenzene. The catalytic activity was found to depend on the Pd loading for all reactions. For the hydrogenation of 1-pentyne, the catalytic performance was strongly affected by the pretreatment procedure and the interlamellar Pd content of the catalyst. The sample with the highest Pd loading was the most efficient catalyst. For the Heck coupling reactions, the $PdCl_2(TDA)_2/GO$ samples proved to be highly active and selective catalysts. The activities of the samples with higher Pd loadings exceeded those reported for conventional heterogeneous Pd catalysts under similar experimental conditions.

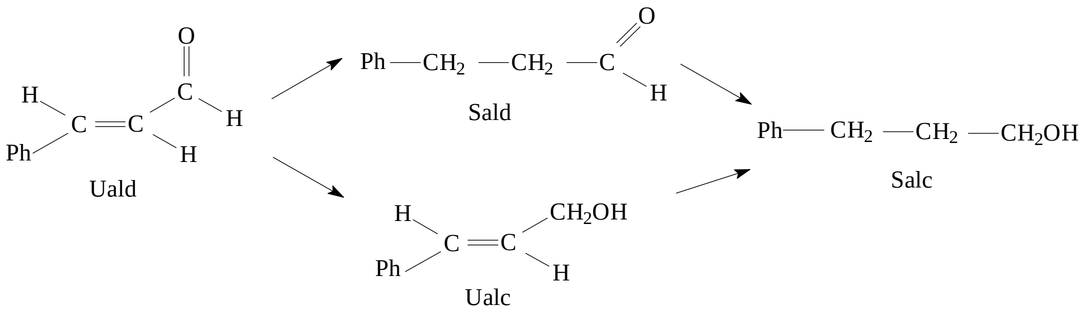
2014 – Our original research plan for the third year was the syntheses of chiral Ru and Rh biphosphine complexes and the application of these complexes in the enantioselective hydrogennation of α,β-unsturated carbonyl compounds. We were planning to study specifically the “ligand effect“ with a series of bidentate biphosphines Ru complexes. All these catalysts would be planned to immobilise to achieve their simple recovery after the reaction. However the research activity was followed a slightly different direction, since we have already had several important results on the catalytic transfer hydrogenation of various aldehydes and ketones we became interested in the catalytic transfer hydrogenation of α,β-unsaturated aldehydes.

With the aim of developing active, chemoselective heterogeneous catalysts, we have prepared the anchored $[\{RuCl_2(TPPMS)_2\}_2]$ and $[RuCl_2(PPh_3)_3]$ catalysts, and applied in the hydrogenation of *trans*-cynnamaldehyde. Fe(Pc), as a new, efficient, heterogeneous catalyst for catalytic transfer hydrogenation of carbonyl funtionality were also developed. The heterogenized version of this complex was prepared and applied in the CTH reaction of *trans*-cinnamaldehyde. In this contribution we want to compare the performance of the two systems, emphasizing the selectivity issue.

The properties of the heterogenized catalysts, $[\{RuCl_2(TPPMS)_2\}_2]$/PTA/NaY and $[RuCl_2(PPh_3)_3]$/PTA/NaY were investigated in the hydrogenation of *trans*-cinnamaldehyde. Using homogeneous complexes under H_2 a pH-dependent equilibrium was found to be exist between the monohydrido $[HRuCl(TPPMS)_3]$ and dihydrido $[H_2Ru(TPPMS)_4]$ derivatives. These two Ru-hydrides have different selectivities in the hydrogenation of α,β-unsaturated aldehydes. Namely, the monohydrido derivative hydrogenates the C=C double bond, while the dihydrido species is a selective catalyst for the hydrogenation of the C=O double bond [12]. Consequently, simply adjusting the pH of the aqueous phase can change the selectivity of the hydrogenation of *trans*-cinnamaldehyde.

Selective hydrogenation of C=O bonds

For the hydrogenation reaction we have applied two slightly different conditions, based on the results obtained under homogeneous conditions [15]. In our ethanolic solutions the basicity was adjusted by Et_3N. For the C=O reduction, basic conditions were applied (see Experimental). The catalyst mixture was prehydrogenated for sufficient time to ensure the formation of the catalytically active Ru-hydrides. The products of the reaction are shown on Scheme 1 (no other products were found during the hydrogenation reaction), and the results are collected in Table 1.



Scheme 1. The hydrogenation reaction of *trans*-cinnamaldehyde.

Abbreviations: Uald = unsaturated aldehyde (*trans*-3-phenylprop-2-enal), Sald = saturated aldehyde (3-phenylpropanal), Ualc= unsaturated alcohol (3-phenylprop-2-en-1-ol), Salc = saturated alcohol (3-phenylpropan-1-ol)

Table 1. The product distribution of the hydrogenation of *trans*-cinnamaldehyde on homogeneous and heterogenized Ru-phosphane catalysts under basic conditions.

catalysts	conversion (%)	TOF (h^{-1})	products distribution		
			Sald	Salc	Ualc
[H_2Ru(TPPMS)$_4$]	68.4	8.5	9.1	0	**90.9**
[H_2Ru(TPPMS)$_4$]/NaY	15.0	38.3	12.0	0	**88.0**
[H_2Ru(PPh$_3$)$_3$]	93.9	11.7	5.5	11.6	**82.9**
[H_2Ru(PPh$_3$)$_3$]/NaY	92.3	11.9	3.0	11.9	**85.1**

Reaction conditions: 0.4 MPa H_2, 65 °C, 0.05 mmol PPh_3 or TPPMS, 0.04 mmol Et_3N, 0.396 mmol substrate, 10.28 µmol (2a) or 0.6 µmol (2a/NaY), 10.42 µmol (2b), 10.89 µmol (2b/NaY). [H_2Ru(TPPMS)$_4$] **(2a)** [H_2Ru(PPh$_3$)$_3$] (**2b**)

It is seen that the heterogenized catalysts – both the sulfonated and the nonsulfonated derivatives - were active in the hydrogenation of *trans*-cinnamaldehyde in alcoholic solution. Comparing the TOF of the heterogenized and the homogeneous catalysts, the heterogenized catalysts have about the same or higher activity than the homogeneous analogs. The higher

catalysts have about the same or higher activity than the homogeneous analogs. The higher

activity of (**2a**)/NaY is in a good agreement with our earlier findings [22], i.e. that the heterogenized catalysts showed about the same or higher reaction rate than the homogeneous counterparts, leading to higher specific activities than those of the homogeneous analogs. Indeed, in the present experiments, the sulfonated derivative had substantially higher specific activity than its homogeneous counterpart while with the PPh_3-containig derivatives no difference could be seen (Table 1).

Considering the selectivity in the above conditions all the catalysts have a fairly good selectivity for the C=O hydrogenation. In other words, the synthetically important product, the unsaturated alcohol, is formed in high yields.

Catalytic transfer hydrogenations of trans-cinnamaldehyde

Applying the developed catalytical system we have examined the CTH reaction of *trans*-cinnamaldehyde. With this study the following questions supposed to be answered: Is the CTH reaction work for α,β-unaturated aldehyde? Is there any selectivity in this reaction? Is it possible to change the selectivity by changing the conditions?

The CTH reaction of α,β-unaturated aldehydes were study in the same conditions what was optimized for aldehydes and the obtained results are collected in Table 5.

Table 2. Fe(Pc) catalysed CTH reaction of *trans*-cinnamaldehyde

Catalyst	**Conversion (%)**	**Product distr. (%)**		
		Ualc	**Sald**	**Salc**
Fe(Pc)	67.2	**44.5**	12.9	42.5
Fe(Pc)/Al_2O_3	58.3	**38.1**	0	61.0
Fe(Pc)	65.3	**44.1**	14.6	41.2
Fe(Pc)/Al_2O_3	56.5	**37.5**	0	62.0

Reaction conditions:4 h , **80** ^{o}C, 2 ml *i*-propanol, 0.0038 mmol Fe(Pc), 0.38 mmol aldehyde, 0,095 mmol NaOH

Data in Table 5. show that the CTH reaction works for α,β-unsaturated aldehydes, too. Some chemoselectivity was observed, since the major product is the unsaturated alcohol, using the original conditions for the catalytic transfer hydrogenation. In this reaction system the cinnamyl alcohol is the most valuable product, so the CTH reaction produces some selectivity, more than 40%, regarding the most valuable product. Considering the heterogenized catalyst, it was active as well, but its activity was smaller than the activity of the free complex. Even the selectivity has changed, no C=C hydrogenation was observed and the ration of the unsaturated alcohol was smaller. Consequently on heterogenized catalyst the saturated alcohol became the major product.

Since were interested in changing the selectivity, we have run the CTH reaction of *trans*-cinnamaldehyde, applying more basic condition , using double amount of NaOH (Table 3).

Table 3. Fe(Pc) catalysed CTH reaction of *trans*-cinnamaldehyde in more basic condition

Catalyst	**Conversion (%)**	**Product distr. (%)**		
		Ualc	**Sald**	**Salc**
Fe(Pc)	100	**72.5**	11.4	16.0
Fe(Pc)/Al_2O_3	100	**77.9**	0	22.0
Fe(Pc)	100	**73.8**	10.3	15.7
Fe(Pc)/Al_2O_3	100	**80.2**	0	19.8

Reaction conditions:4 h , **80** ^{o}C, 2 ml *i*-propanol, 0.0038 mmol Fe(Pc), 0.38 mmol aldehyde, 0,19 mmol NaOH

Table 3. shows that changing the conditions the selectivity has changed, as well. As a matter of fact the selectivity has increased towards the most valuable product, the unsaturated

alcohol. The other important observation is that we have reached full conversion on both type of catalysts. On heterogenized complex a similar trend was observed as in the former case, namely the saturated aldehyde has not formed and consequently the selectivity of the most valuable product increased, close to 80 %.

Recycling of immobilized catalysts

The most important advantage of immobilization is the possibility of recycling, which is a crucial point if the complex is expensive or difficult to get it. The applied Ru-phosphane complexes are expensive, so we have checked the recyclability of these complexes (Figure 2.)

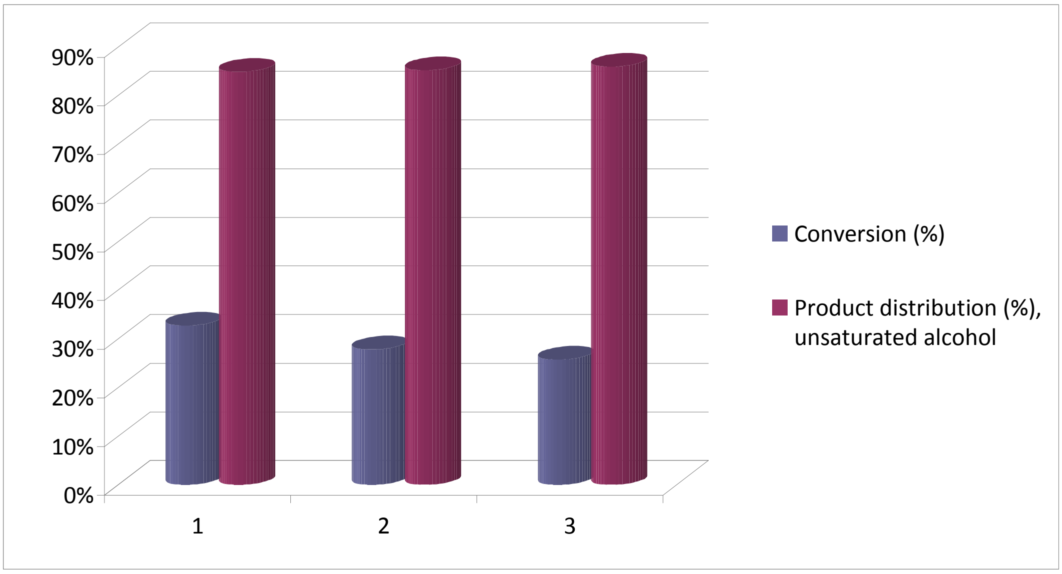


Figure 1. The product ditribution for three subsequent runs of the hydrogenation of *trans*-cinnamaldehyde on **(2b)/NaY** catalyst.

As Figure 1. clearly show, we could recycle the catalyst in three subsequent runs without any significant change in conversion and selectivity.

Considering the iron system, Fe(Pc) is a readily available, inexpensive material so we have not invetigated the recyclability. However the heterogenized version of this system must be recyclable according to our former experience.

With the final goal of developing a „state-of-the-art" hydrogenation catalyst, which made from inexpensive materials, easy to synthesize and convenient to handle we have prepared the immobilized version of Fe(Pc) and applied in the CTH reactions of aldehydes. In this work we have compared the application of heterogenized Ru-phosphane complexes in the hydrogenation of *trans*-cinnamaldehyde and the catalytic transfer hydrogenation of the same substrate. On anchored Ru(phosphane) catalysts the chemoselectivity was changed by changing the basicity, in basic condition the unsaturated alcohol was the major product, while in acidic condition C=C hydrogenation happened. The anchored Ru(phosphane) complexes was recyclable without any significant change in activity.

The catalytic transfer hydrogenation was performed an inexpensive iron complex [Fe(Pc)] which was proven to be active in the CTH reactions of aldehydes. We have extended the application of this catalyst in this work in the reduction of *trans*-cinnamaldehyde, emphasizing the selectivity issue. Our data show that the catalytic transfer hydrogenation is a valuable tools for reduction of α,β-unsaturated aldehydes, too. Fe(Pc) was proven to be an inexpensive, effective catalyst for the reduction of *trans*- cinnamaldehyde, which is easy to perform and convenient to handle. Even the selectivity is good, using the suitable condition, it can produce the most valuable product, the unsaturated alcohol in a good yield .

Comparing the two possibilities for hydrogenation we can establish that the CTH reaction could be a real alternative of reduction: it is effective, convenient to handle and works for α,β-unsaturated aldehydes, too. In spite of the fact that we could not reached the chemoselectivity of the Ru(phospane) system, the other advantages of the CTH reaction makes it applicable in organic laboratory.