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**HETEROGENEOUS METAL-CATALYSED C-C COUPLING
REACTIONS: RESEARCH & DEVELOPMENT**

Summary of PhD Thesis

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1. Introduction

Nowadays the development of new catalysts came into the limelight. These materials are preferably more active, more selective, favourably recoverable, easier to handle and environmentally more benign than classic substances. The supported heterogeneous catalysts possess several advances in fine chemistry. Their applications in batch reactions have the advantage of easy separation by a simple filtration from the reaction medium, which makes the technology simple, short and economic. The easy recovery of the catalytic material facilitates reuse or recycling. Therefore the synthetic applications of heterogeneous supported catalysts result in a green and economic process.

At the University of Poitiers in the Institute of Chemistry of Poitiers: materials and natural resources (IC2MP) extensive research is focused on the development and application of supported metal catalyst. At the Budapest University of Technology and Economics in the research group of the Department of Organic Chemistry and Technology the application of heterogeneous catalysts in organic syntheses has been studied. In the framework of my thesis the knowledge of the two research groups were combined resulting at a complementary and comprehensive study including: the preparation of Cu-Pd bimetallic catalysts, the study of the effect of the support, the characterisation, application of these catalysts in organic reactions, a kinetic study, the reuse of the catalysts, the characterisation of the recovered catalysts and the explanation of the catalytic activity and stability thanks to the surface analytic methods.

2. Review of the literature

In heterogeneous catalysis one, two or more metals can be introduced on the support resulting the formation of monometallic, bimetallic and multimetallic catalysts, respectively. Compared to monometallic catalysts, bimetallic or multimetallic catalysts may show an increased selectivity or better resistance to deactivation. The surface state of bimetallic catalysts depends strongly on the preparation and activation procedures.

Metal catalysis has a dominant role in the modern organic chemistry. In particular, cross-coupling reactions allow bond formations, which have previously been impossible to perform^{1,2}. Buchwald et al. reported that reactions with FeCl₃ may in certain

¹ A. de Meijere, F. Diederich, Metal-Catalyzed Cross-Coupling Reactions, 2nd Ed. Wiley, Weinheim 2004.

cases be significantly affected by trace quantities of other metals, particularly copper³. Research interest in bimetallic catalysts is mainly due to their tuneable chemical/physical properties by a number of parameters like composition and morphostructure⁴. Compared to monometallic catalysts, bimetallic or multimetallic catalysts may show better performances as it concerns activity, selectivity and stability. In the literature numerous bimetallic catalysts have been shown to exhibit unique properties which are different from those of their monometallic counterparts⁵.

Coupling reactions are efficient tools for the coupling of organic compounds by the help of metal catalysts. Two or more compounds can be coupled to target the desired product. An important group of these reactions results in novel carbon-carbon bond formation. The importance of cross coupling reactions was confirmed in 2010 when the Nobel Prize in Chemistry was awarded jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki 'for palladium-catalyzed cross couplings in organic synthesis'. Even though from time to time several efficient, selective, stable, and relatively cheap methods emerge, carbon-carbon coupling reactions stay in the centre of attention; and research interest focuses on the development of catalytic systems for such reactions. The Suzuki coupling is a palladium-catalysed cross-coupling reaction between organoboron compounds and organic halides or triflates (Figure 1).

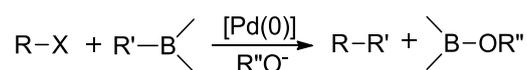


Figure 1. General scheme of the *Suzuki–Miyaura* coupling

It serves as an important tool for biaryl synthesis. Biaryl units are present in natural products, pharmaceuticals, herbicides, conducting polymers, liquid crystals and molecular wires⁶. The *Suzuki–Miyaura* coupling provides a facile, selective way to a wide range of products. Mild reaction conditions are applied and the reaction partners are easily available molecules. Moreover, the inorganic by-product of the reaction is non-toxic and easily removable from the reaction mixture thereby making the Suzuki cou-

² J.-P. Corbet, G. Mignani, *Chem. Rev.* 106 (2006) 2651-2710.

³ S.L. Buchwald, C. Bolm, *Angew. Chem. Int. Ed.* 48 (2009) 5586-5587.

⁴ Z. Wei, J. Sun, Y. Li, A.K. Datye, Y. Wang, *Chem. Soc. Rev.* 41 (2012) 7994-8008.; J. Mao, Y. Liu, Z. Chen, D. Wang, Y. Li, *Chem. Commun.* 50 (2014) 4588-4591.; M. Sankar, N. Dimitratos, P.J. Miedziak, P.P. Wells, C.J. Kiely, G.J. Hutchings *Chem. Soc. Rev.* 41 (2012) 8099–8139.

⁵ B.T. Meshesha, N. Barrabés, J. Llorca, A. Dafinov, F. Medina, K. Föttinger, *Appl. Catal. A* 453 (2013) 130-141.; F. Gauthard, F. Epron, J. Barbier, *J. Catal.* 220 (2003) 182-191.; E.M. Crabb, R. Marshall, *Appl. Catal. A* 217 (2001) 41-53.

⁶ S.P. Stanforth, *Tetrahedron* 54 (1998) 263-303.; S. Paul, J.H. Clark, *Green Chem.* 5 (2003) 635-638.

pling suitable not only for laboratories but also for industrial processes⁷. Since the first publication of this reaction⁸ several attempts were made and a great number of publications and reviews were released reporting homogeneous and heterogeneous mostly palladium-catalysed pathways to perform this coupling.

Only a few examples were published for this coupling concerning Cu-Pd bimetallic catalysts. As a homogeneous route Cu₂O was proved to be a remarkable co-catalyst in the Pd(PPh₃)₄ catalysed reaction of arylboronic acids with ethyl bromoacetate.⁹ Furthermore a Suzuki-type C-H arylation of azoles was reported with Pd(OAc)₂, Cu(OAc)₂ and CuCl¹⁰. The beneficial effect of the CuCl was reported for the Pd(OAc)₂ catalysed Suzuki coupling of 2-heterocyclic boronates¹¹. Liebeskind et al. reported a palladium catalysed copper mediated route for the coupling of aryl and alkenyl iodides and arylboronic acids in the absence of base with copper(I) thiophene-2-carboxylate as mediator¹². The use of a copper based support proved also to be suitable as Pd nanoparticles supported on CuO were described as efficient catalyst for the reaction¹³. The application of copper nanoclusters and Cu/Pd nanoclusters have also been reported for this reaction¹⁴. In a patent Pd/Cu colloids in different molar composition were examined and it was found that the Pd(50%)/Cu(50%) composition was the most efficient¹⁵. The metal loadings in these reactions are generally 5 mol% Pd-salt and 10-100 mol% Cu-salt.

As Pd appears to be active for Suzuki coupling, it was chosen for our study. Due to its costs and according to bibliography concerning the beneficial effect of copper, we decided to mix Pd and Cu. Our aim was to use the noble metal in lower quantity along with a higher amount of the inexpensive transition metal. So that the metal loading was selected to be 0.2 mmol Pd and 1 mmol Cu / 1 g support. The way of preparation was chosen to be wet impregnation as it is a simple, economic and reproducible method permitting the possible proximity of the two metals. The supports were decided according to previous studies on the excellent activity of Cu-4A in several organic transforma-

⁷ A. Suzuki, *J. Organomet. Chem.* 576 (1999) 147-168.

⁸ N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* 20 (1979) 3437-3440.; N. Miyaura, A. Suzuki, *J. Chem. Soc. Chem. Commun.* (1979) 866-867.

⁹ X.-X. Liu, M.-Z. Deng, *Chem Commun.* (2002) 622-623.

¹⁰ B. Liu, X. Qin, K. Li, X. Li, Q. Guo, J. Lan, J. You, *Chem. Eur. J.* 16 (2010) 11836-11839.

¹¹ J.Z. Deng, D.V. Paone, A.T. Ginnetti, H. Kurihara, S.D. Dreher, S.A. Weissman, S.R. Stauffer, C.S. Burgey, *Org. Lett.* 11 (2009) 345-347.

¹² C. Savarin, L.S. Liebeskind, *Org. Lett.* 3 (2001) 2149-2152.

¹³ K. Chattopadhyay, R. Dey, B.C. Ranu, *Tetrahedron Lett.* 50 (2009) 3164-3167.

¹⁴ M.B. Thathagar, J. Beckers, G. Rothenberg, *J. Am. Chem. Soc.* 14 (2002) 11858-11859; M.B. Thathagar, J. Beckers, G. Rothenberg, *Adv. Synth. Catal.* 345 (2003) 979-985.

¹⁵ J.A. Coggan, N.-X. Hu, H.B. Goodbrand, T.P. Bender US Patent 2006/0025303 (2006)

tions¹⁶ and on the acido-basic properties on the MgO-Al₂O₃ mixed oxides¹⁷.

3. Experimental methods

The catalysts characterisation was carried out in the Institute of Chemistry of Poitiers: materials and natural resources (IC2MP). The metal content on the support was determined by ICP-OES. Specific surface areas of samples were measured by BET surface analyser. X-ray powder diffraction (XRD) was carried out to gain information on the morphology of the catalysts. Dispersion of Cu and Pd particles on the surface of the supports were identified by TEM-EDS. The distribution and reducibility of Cu and Pd particles were investigated via H₂-TPR experiment. Basicity was measured by adsorption of carbon dioxide followed by FT-IR analysis of the sample.

The organic products were identified using ¹H NMR and ¹³C NMR spectroscopy and/or GC-MS measurements. The melting point of solid samples was also measured and compared with published data.

4. New scientific results

4.1. Cu-Pd 4A supported bimetallic catalysts for the Suzuki–Miyaura coupling

A new, simple method was found to perform the *Suzuki–Miyaura* coupling. A full study was made including the catalyst preparation, characterisation, application in the coupling, reuse of the catalyst, the characterisation of the recovered catalyst and the explanation of the catalytic activity and stability thanks to the surface analysis. The importance of the catalyst preparation method was proven.

Four catalysts were prepared with wet impregnation: Cu-4A, Pd-4A as monometallic catalysts and Cu-Pd-4A bimetallic catalysts. The bimetallic catalysts were prepared in two ways: by the Two-Step Impregnation (TSI) of the precursors Cu-Pd-4A-TSI was obtained and Co-Impregnation (CI) of the two metal salts yielded Cu-Pd-4A-CI bimetallic catalysts. By the use of co-impregnation, we favour the formation of an alloy while during successive impregnation copper had enough time to form pure particles

¹⁶ A. Fodor, Á. Kiss, N. Debreczeni, Z. Hell, I. Gresits, *Org. Biomol. Chem.* 8 (2010) 4575-4581.; Á. Kiss, Z. Hell, *Synth. Commun.* 43 (2013) 1778–1786.; Á. Kiss, Z. Hell, *Tetrahedron Lett.* 52 (2011) 6021–6023.; A. Kiss, Z. Hell, *Synfacts* 8 (2012) 0105.

¹⁷ C. Poupin, R. Maache, L. Pirault-Roy, R. Brahmi, C.T. Williams, *Appl. Catal. A* 475 (2014) 363–370.

before the addition of Pd. The catalysts were characterised by ICP, BET, XRD, TEM, EDS and TPR. We found that the metal content of the catalyst was corresponding to the targeted values. TSI has a higher surface area compared to CI. From DRX, information was hard to gain due to the predominant characteristic diffractogram of the support, however the signals of Cu-Pd crystals were found. From the TEM analysis we concluded the presence of bimetallic alloys. The composition of these alloys was different. On TSI the Cu and Pd ratio was equal, while on CI copper-rich crystals were present. The average particle size did not differ notably in the catalysts prepared with two methods (Figure 2).

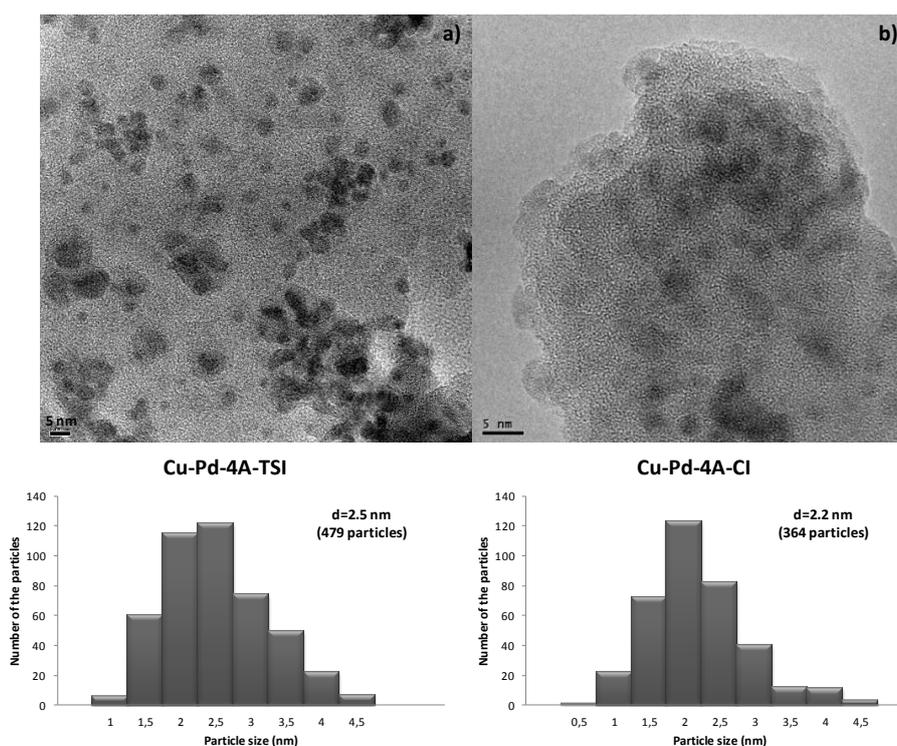


Figure 2. TEM image of the fresh catalysts: a) well dispersed particles on Cu-Pd-4A-TSI; b) well dispersed particles on Cu-Pd-4A-CI; particle size distribution of Cu-Pd-4A-TSI and Cu-Pd-4A-CI

The TPR analysis revealed the different interaction between the two metals on the support in case of TSI and CI. Comparing the two TPR profiles the peaks were shifted and new peaks occurred proving the different properties of the two materials. Based on the results of catalysis characterisation one can conclude that the two metals were brought to close interaction with wet impregnation which in certain cases can be unsatisfactory for merging the metals.

The applicability of the surface analyzed catalysts was examined in the *Suzuki–Miyaura* cross-coupling reaction. The activity as well as the stability of the bimetallic

catalysts was confronted with the monometallic counterparts'. As a Suzuki model reaction, we selected the reaction of phenylboronic acid (**1a**) with iodobenzene (**2a**) in the presence of potassium carbonate as base in ethanol as solvent (Figure 3).

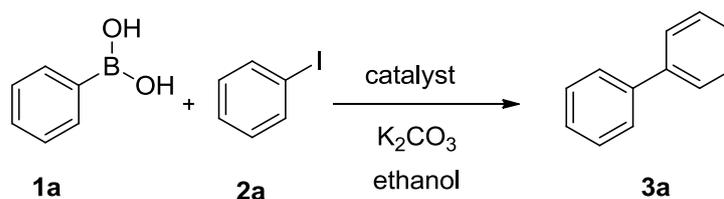


Figure 3. The Suzuki–Miyaura coupling of phenylboronic acid (**1a**) and iodobenzene (**2a**)

To select the most suitable catalyst to perform the reaction both the monometallic catalysts and the bimetallic catalysts were examined. The results obtained for the different catalysts are summarised in Table 1.

Table 1. Catalyst selection for the reaction of iodobenzene (**2a**) with phenylboronic acid (**1a**)^a

Catalyst	Yield (%) ^b	Conversion (%) ^c	TOF (h ⁻¹) ^d
Cu-4A	- (6%) ^e	62%	n/a
Pd-4A	93%	100%	n/a
Pd-4A (second cycle)	66%	97%	n/a
Cu-Pd-4A-TSI	>99%	100%	23.3
Cu-Pd-4A-TSI (second cycle)	>99%	100%	n/a
Cu-Pd-4A-CI	>99%	100%	22.6
Cu-Pd-4A-CI (second cycle)	>99%	100%	n/a

^aReaction conditions: phenylboronic acid (**1a**) (1.5 mmol), iodobenzene (**2a**) (1 mmol), potassium carbonate (3 mmol), 0.1 g catalyst (2 mol% Pd and/or 9 mol% Cu) in EtOH, 78 °C, 1 h

^bIsolated yield

^cConversion of iodobenzene (**2a**)

^dAt 1 hour, calculated assuming that the number of the atoms on the surface is the amount of the catalyst active phases. Ignoring the exact repartition between Cu and Pd, the average of the two values D x d corresponding to each metal was used

^eAccording to GC-MS analysis of the reaction mixture

The monometallic catalyst Cu-4A is not suitable for the coupling reaction. Pd-4A seemed to be a good catalyst for the reaction as good yield (93%) for biphenyl (**3a**) was obtained. The activity of the catalyst decreased significantly after the second use where biphenyl (**3a**) was provided only by 66% yield. On the contrary, Cu-Pd-4A catalysts prepared by either method remained efficient during two cycles resulting in biphenyl (**3a**) production with quantitative yield. The difference between the two bimetallic catalysts was shown after the sixth usage as the CI catalyst gave the product only with good, 80% yield, compared to >99% obtained from the reaction of TSI catalyst. The characterisation of these six times used catalysts by ICP-OES, XRD and TEM-EDS allowed us to conclude that this loss of activity of the CI catalyst was due to the absence

of Cu-Pd 1:1 alloy, the presence of Cu-rich Cu-Pd species and the growth of the particle size. Thus we found that a Cu-Pd alloy with atom ratio 1:1 is responsible for the catalytic activity.

To examine the scope of the reaction experiments were carried out with different aryl halides in the presence of TSI catalyst. Aryl bromides showed good activity and low activity of aryl chlorides were shown. Selectivity between halides was also observed. Furthermore a series of substituted biphenyls were synthesized starting from substituted boronic acids and iodobenzene or bromobenzene derivatives in the presence of the bimetallic Cu-Pd-4A-TSI catalyst. The *m*- and *p*- substituted derivatives gave excellent yield, while *o*-substituted derivatives gave weaker results because of steric effects. No significant electronic effect was observed. Substituted biphenyls from two or three pathways were achieved at least with good yields. Excellent yields were resulted in *ortho*-, *meta*-position with substituted boronic acid, while in *para*-position with aryl halides. Aliphatic boronic acids didn't undergo the coupling.

4.2. Cu-Pd MgAlO supported bimetallic catalysts for the Suzuki–Miyaura coupling

Our study was continued with a support having stronger basic character than the previously used 4A. Our choice was MgO-Al₂O₃ with Mg:Al 3:1 ratio (MgAlO) as support to examine since it showed promising properties in a previous study.¹⁷ Wet impregnation was selected as preparation for the catalysts studied: Cu-Pd-MgAlO-TSI and Cu-Pd-MgAlO-CI. The catalysts were characterised by ICP, BET, XRD, TEM, EDS, TPR and FT-IR.

According to XRD analysis besides the signals of the supports CuPdO₂ particles were found in majority on the surface of both CI and TSI catalysts. According to TEM results the particle size was heterogeneous in both cases. Small particles with an average size of 1.9 nm and narrow size distribution (0.7-4.4 nm) were present on the surface of CI. The larger particles were up to 45 nm, and the overall average particle size was 15.6 nm. These two populations were also present on TSI but with wider size distribution as the smaller particles were between 1-10 nm with an average size of 4.9 nm. However the overall distribution is larger and an important amount of particles between 10-50 nm can be pointed out on CI whereas on TSI a bimodal distribution can be seen with small particles and very big particles. Thus, the average size of particles is higher on TSI than on CI (49 nm vs 15.6). By EDS analysis the presence of Cu/Pd 1:1 was proven on both catalysts. Comparing the two TPR profiles the interaction of the two

metals were proven and also the presence of different monometallic particles on the two catalysts. The reduction peaks shifted compared to those of the monometallic catalysts indicating the proximity of the two metals.

The basic properties of the two supports (4A, MgAlO) and the two most stable Cu-Pd catalysts (Cu-Pd-4A-TSI, Cu-Pd-MgAlO-CI) were studied by the adsorption of carbon dioxide followed by FT-IR. Our aim was to ascertain the differences in basicity and to study how the impregnation affects the basic characteristics of the supports. To obtain quantitative information on the basicity among these four materials the bands corresponding to bidentate carbonates generally related to basicity were taken in account between 1670 cm^{-1} and 1310 cm^{-1} (Figure 4).

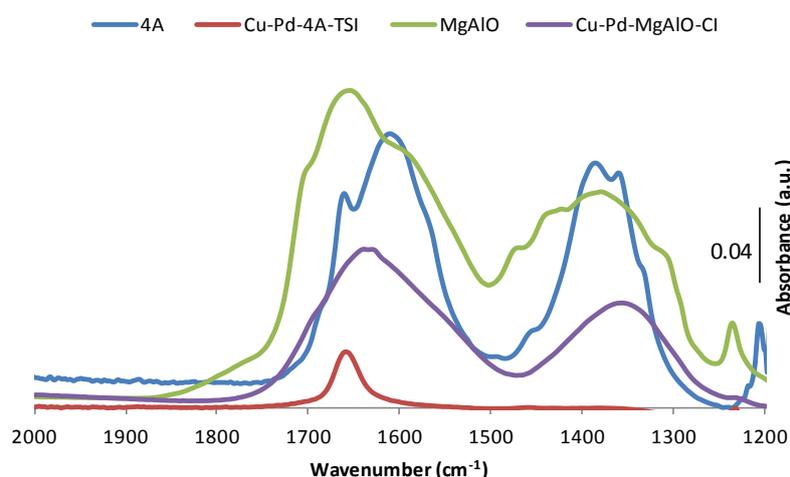


Figure 4. Subtracted spectra after evacuation at room temperature of 20 mg material

The density of basic hydroxyl groups showed that MgAlO and Cu-Pd-MgAlO-CI exhibit significantly stronger basic properties than 4A or Cu-Pd-4A-TSI. We concluded from the FT-IR study that the ranking of the materials based on their basic properties (area per m^2) is as follows:



The Cu-Pd-MgAlO catalysts were tested in the reaction of phenylboronic acid (**1a**) with iodobenzene (**2a**) in the presence of potassium carbonate as base in ethanol as solvent (Figure 3). In the first experiments these catalysts showed the same activity as the Pd-Cu-4A catalysts earlier, the corresponding product – biphenyl (**3a**) – was obtained with quantitative preparative yield.

The stability of the catalysts was also studied. The activity of the catalyst prepared with CI did not change even after 6 catalytic runs, while the samples prepared with TSI

5. Theses

1. A new bimetallic palladium/copper catalyst was developed by successive impregnation (TSI) and co-impregnation (CI) on 4Å molecular sieve (4A) support. The catalyst characterisation methods showed that the two metals (Cu, Pd) were brought into close interaction on the surface of the support and that the method of impregnation had an impact on the surface properties of the catalysts. The activity of the catalysts was tested in the *Suzuki–Miyaura* reaction of phenylboronic acid and iodobenzene and it was observed that while the Cu-Pd-4A-TSI catalyst kept its activity during six cycles that of the Cu-Pd-4A-CI dropped. The characteristics of the six times used catalysts (TEM-EDS, ICP-OES, XRD) showed that a Cu–Pd alloy with atomic ratio 1:1 was responsible for the catalytic activity and stability. It was established that the role of Cu in the *Suzuki–Miyaura* reaction was the stabilisation of the palladium due to Pd–Cu interaction, thus Pd could keep its active form.^[D1]

2. Studying the effect of the substituents on the boronic acids and aryl halides in the Cu-Pd-4A-TSI catalysed *Suzuki–Miyaura* reaction, excellent yields were obtained in *ortho*- and *meta*-position with substituted boronic acid derivatives, while in *para*-position with aryl halides. To compare iodo- and bromobenzenes we concluded that in certain cases higher yields could be achieved with bromobenzenes than with iodobenzenes.^[D2]

3. During the study of the effect of different supports (4A, MgAlO) on the characteristics and catalytic activity of the copper-palladium bimetallic catalysts it was found that the catalyst prepared with CI, containing Cu/Pd 1/1 alloy in majority with smaller particle size proved to be stable even for six runs contrary to TSI. This observation confirms that whatever the way of preparation or the support, the key-point is the presence of Pd-Cu 1:1 particles to enhance the catalytic performances. A crucial difference between the MgAlO and 4A supported catalyst was found in the reaction time necessary for the *Suzuki–Miyaura* reaction. With the Cu-Pd-MgAl-CI catalyst the reaction time could be reduced to thirty minutes contrary to one hour with Cu-Pd-4A-TSI for the complete conversion of iodobenzene to biphenyl. Moreover it was concluded that with a more basic support the reduction of the quantity of the base was possible however it brought slightly decreasing yield.^[D3]

4. The Petasis-borono Mannich reaction of salicylaldehyde, morpholine and phenylboronic acid was performed in the presence of each mono- and bimetallic

catalysts. While the conversion of salicylaldehyde was mostly over 90%, the product formation with the highest purity was achieved with MgAlO (support), Cu-4A and Cu(0.2)-4A.

6. Application of the scientific results

The replacement of the homogeneous catalysts by heterogeneous catalysts is favoured in fine chemical organic syntheses. In this comprehensive study two active, selective and reusable catalysts were presented for application in the *Suzuki–Miyaura* cross coupling reaction. This reaction enables the production of wide range of products as presented in the framework of this thesis. This Cu-Pd bimetallic catalyst facilitated reaction might serve in the syntheses of molecular libraries. It is important to highlight that the determination of the catalytically active phase in the Suzuki reaction makes the preparation of fine-tuned catalysts possible.

7. Publications

Full scientific publications related to the PhD Thesis

- [D1] **A. Fodor**, Z. Hell, L. Pirault-Roy, Copper(II)- and palladium(II)-modified molecular sieve, a reusable catalyst for the Suzuki-Miyaura-coupling, *Appl. Catal. A* 484 (2014) 39-50. (IF: 3.942; I.c.: 3)
- [D2] **A. Fodor**, Á. Magyar, D. Barczikai, L. Pirault-Roy, Z. Hell, Study of the structure-activity relationship in a heterogeneous copper-palladium catalysed Suzuki-Miyaura coupling, *Catal. Lett.* 145 (2015) 834-839. (IF: 2.307)
- [D3] **A. Fodor**, Z. Hell, L. Pirault-Roy, The influence of the nature of the support on the copper - palladium catalysed Suzuki-Miyaura-coupling, *Catal Lett.* – submitted article (IF: 2.307)
- [D4] N. Debreczeni, **A. Fodor**, Z. Hell, Coupling of boronic acids with amines in the presence of a supported copper catalyst *Catal. Lett.* 144 (2014) 1547-1551. (IF: 2.307)

Further published articles

- [5] **A. Fodor**, Á. Kiss, N. Debreczeni, Z. Hell, I. Gresits, A simple method for the preparation of propargylamines using molecular sieve modified with copper(II), *Org. Biomol. Chem.* 8 (2010) 4575–4581. (IF: 3.451; I.c.: 20)
- [6] **A. Fodor**, Investigation of mineral-type catalyst modified with metal ions in organic syntheses (TDK abstract), *Per. Pol. Chem. Eng.* 54 (2010) 49-50. (IF: 0)

- [7] A. Takács, **A. Fodor**, J. Németh, Z. Hell, Zeolite Catalysed Method for the Preparation of 2,3-dihydroquinazolin-4(1H)-ones, *Synth. Commun.* 44 (2014) 2269-2275. (IF: 0.929)
- [8] **A. Fodor**, J. Németh, Z. Hell, Application of a clinoptylolite-type zeolite in the synthesis of different heterocycles, *Curr. Green Chem.* 1 (2014) 249-256. (IF: 0)
- [9] Á. Kiss, J. Németh, **A. Fodor**, Z. Hell, Supported metal catalysts in organic syntheses, *Per. Pol. Chem. Eng.* 59 (2015) 72-81. (IF: 0.296)

Oral presentations

- [10] **Fodor A.**; Kiss Á.; Hell Z. Fémionokkal módosított, ásványi típusú katalizátorok vizsgálata szerves szintézisekben - XXXIV. Kémiai Előadói Napok, Szeged, 2011.
- [11] **Fodor A.**; Magyar Á., Hell Z., Pirault-Roy L.: Heterogén kétfémes katalizátorok előállítása, felületi vizsgálata, alkalmazása szerves szintézisekben – Oláh György Doktori Iskola XI. konferenciája, Budapest, 2014.
- [12] **A. Fodor**; Z Hell, L. Pirault-Roy: Synthèse de composés organiques à l'aide de catalyseurs hétérogènes – GECat 2015 – Domaine Saint-Jacques (Obernai), 26-29. May 2015.

Poster presentations

- [13] **Fodor A.**, Debreczeni N., Hell Z.: Fémionokkal módosított bázikus karakterű anyagok vizsgálata szerves szintézisekben – Oláh György Doktori Iskola IX. konferenciája, Budapest, 2012.
- [14] **A. Fodor**, Z. Hell, L. Pirault-Roy: Investigation of Mineral Type Bases Modified with Metal Ions: Preparation and characterization – Oláh György Doktori Iskola X. konferenciája, Budapest, 2013.
- [15] **Fodor A.**, Debreczeni N., Hell Z., Pirault-Roy L.: Fémionokkal módosított bázikus karakterű anyagok vizsgálata: előállítás, jellemzés és alkalmazás szerves szintézisekben – Vegyészkonferencia Hajdúszoboszló, 26-28. June 2013.
- [16] **A. Fodor**, N. Debreczeni, Z. Hell, L. Pirault-Roy: Investigation of mineral type catalysts modified with metal ions: preparation, characterization and application in organic synthesis – 11th European Congress on Catalysis – EuropaCat-XI, Lyon, 1-6. September 2013.
- [17] **A. Fodor**, Z. Hell, L. Pirault-Roy: Insight into a heterogeneous bimetallic catalyst's life – from preparation to catalytic tests in organic syntheses; explanation of activity and stability – 5th EuCheMS Chemistry Congress – Istanbul, 31. August-4. September 2014.