Abschlussbericht [‡]

über die Förderung des Forschungsgebietes

Neue Hybridkatalysatoren aus ionischen Flüssigkeiten

und mikro- und mesoporösen Materialien

durch die Max-Buchner-Forschungsstiftung

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1. O. Jimenez, T. E. Müller, J. A. Lercher, Tailoring adsorption / desorption properties of hydroamination catalysts with ionic liquids in Ionic Liquids in Organic Synthesis, ACS Symposium Series 950, edited by Malhotra, ACS, 2006.
2. O. Jimenez, T. E. Müller, C. Sievers, A. Spirkl, J. A. Lercher, *Chem. Comm.*, 2006, 2974-2976: Markownikoff and *anti*-Markownikoff Hydroamination with Palladium Catalysts Immobilized in Thin Films of Silica Supported Ionic Liquids.
3. C. Sievers, O. Jimenez, T. E. Müller, S. Steuernagel, J. A. Lercher, *J. Am. Chem. Soc.*, 2006, **128**, 13990-13991: Formation of solvent cages around organometallic complexes in thin films of supported ionic liquid.
4. C. Sievers, O. Jiménez, X. Lin, T. E. Müller, B. Wierczinski, J. A. Lercher, *J. Mol. Cat. A*, 2007, submitted for publication: Bi-functional catalysts for the direct addition of aniline to styrene

Abstract

The concept of immobilising organometallic complexes in thin films of supported ionic liquid was utilized to generate a new class of hydroamination catalysts. High activities for the addition of aniline to styrene were obtained with a bi-functional system comprising $[Pd(DPPF)](CF_3CO_2)_2$ and CF_3SO_3H immobilised in silica supported imidazolium salts. Detailed characterisation of the catalysts showed that the metal complexes are enclosed in solvent cages of ion pairs of the ionic liquid. Upon increase in temperature, the imidazolium cations gain increasing mobility until the solvent cages break down at a specific temperature, which is noticeable as phase transition. At temperatures below the phase transition, the catalytic activity was strongly influenced by the choice of the ionic liquid. In contrast, at higher temperatures, the activity for formation of the Markownikoff product was similar with different ionic liquids, which was accounted to the breakdown of the solvent cages of ionic liquid. Unexpectedly, the formation of the *anti*-Markownikoff product was also observed.

1. Introduction

Aliphatic and aromatic amines are important intermediates to nitrogen containing molecules, including many pharmaceuticals and agrochemicals. Hydroamination offers one of the most attractive pathways to this class of products, as new CN bonds are formed in a single reaction step from easily accessible alkenes and alkynes [1-3]. Although various homogeneous catalysts are known for hydroamination reactions [e.g., 4-7], only few examples of heterogeneous catalysts have been reported [8]. High activities for inter- and intramolecular hydroamination of alkynes was observed, when catalytically active metal cations (such as Rh^+, Pd^{2+}, Cu^+, Zn^{2+}) were incorporated in zeolite H-Beta. This was accounted to the simultaneous presence of Brønsted acidic hydroxyl groups and Lewis acidic metal cations [9,10]. Apparently, particularly high activities in hydroamination are achieved with bi-functional catalysts. Thus, it seemed highly promising to combine a Lewis acidic metal centre and a Brønsted acid to a bi-functional catalytic system [11]. The concept of supported ionic liquid catalysts [12,13] appeared particularly suitable in this respect. The present work reports on immobilisation of the two functions in a supported film of imidazolium salts and the preparation of well-tailored catalysts for the intermolecular hydroamination of styrene with aniline (Fig. 1).
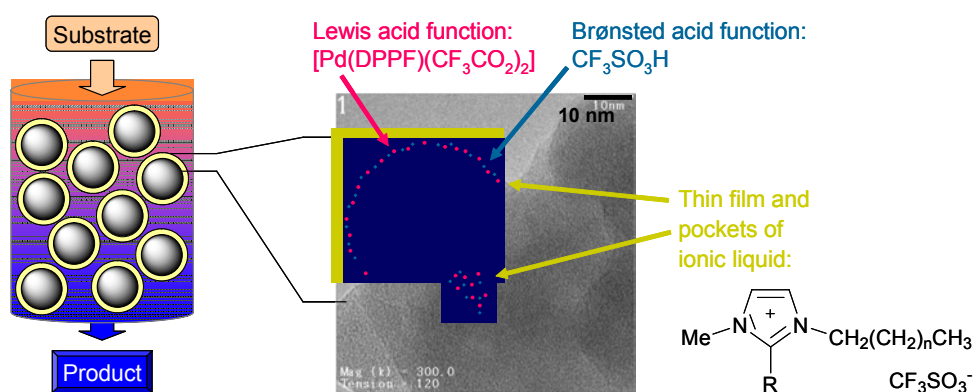

Fig. 1 Concept of immobilizing organometallic complexes in supported films of ionic liquid (R = H, Me; Alkyl = C_2H_5, C_4H_9, C_6H_{13}) for applications in fixed bed reactors and transmission electron micrograph of the catalyst Pd3/EMIm/SiO$_2$.

2. Experimental

Catalysts were prepared by immobilization of [Pd(DPPF)(CF$_3$CO$_2$)$_2$] and CF$_3$SO$_3$H in imidazolium salts (C$_3$N$_2$H$_2$MeRAlkyl)$^+$ CF$_3$SO$_3^-$ supported on silica (Table 1). Four different ionic liquids were used, which provided a series of catalysts Pd/IL/SiO$_2$ with decreasing polarity of the ionic liquid (IL) in the sequence EMIm > BMIm > HMIm > HM$_2$Im.[†] For comparison, a series of reference samples (H$^+$/IL/SiO$_2$) was prepared, for which only the Brønsted acid CF$_3$SO$_3$H was supported in the thin film of the ionic liquid.

Table 1 Catalysts used in this study and selected physicochemical properties

Catalyst	Pd content / wt% (calc.)[3]	BET surface area / m^2·g^{-1}	Pore volume / ml·g^{-1}
SiO$_2$	-	150	0.84
H$^+$/EMIm/SiO$_2$	-	38	0.25
Pd1/EMIm/SiO$_2$	0.11 (0.12)	16	0.15
Pd2/EMIm/SiO$_2$	0.22 (0.23)	12	0.11
Pd3/EMIm/SiO$_2$	0.40 (0.44)	11	0.11
H$^+$/BMIm/SiO$_2$	-	39	0.24
Pd1/BMIm/SiO$_2$	0.11 (0.12)	18	0.14
Pd2/BMIm/SiO$_2$	0.21 (0.24)	16	0.13
Pd3/BMIm/SiO$_2$	0.41 (0.45)	9	0.10
H$^+$/HMIm/SiO$_2$	-	42	0.23
Pd1/HMIm/SiO$_2$	0.14 (0.13)	21	0.20
Pd2/HMIm/SiO$_2$	0.23 (0.24)	17	0.17
Pd3/HMIm/SiO$_2$	0.43 (0.46)	10	0.08
H$^+$/HM$_2$Im/SiO$_2$	-	45	0.25
Pd1/HM$_2$Im/SiO$_2$	0.12 (0.13)	23	0.19
Pd2/HM$_2$Im/SiO$_2$	0.24 (0.24)	19	0.15
Pd3/HM$_2$Im/SiO$_2$	0.41 (0.46)	14	0.10

[3] Determined by neutron activation by X. Lin and B. Wierczinski, Institut für Radiochemie

Tests on catalytic activity in batch mode were performed under inert atmosphere in a Radleys reaction carousel with 12 parallel reactors. The catalyst (0.25 g) was suspended in octane (15 ml) and the mixture heated to reflux at 125°C. Aniline (1.82 ml, 20 mmol), styrene (3.44 ml, 30 mmol) and undecane (1 ml, internal GC standard) were added to each of the reactors. Samples (50 µl) were taken periodically and analyzed by GC to quantify conversion and selectivity of the reaction. For the tests on catalytic activity in continuous operation, a fixed bed reactor with 115 mm length and 3 mm inner diameter was filled with catalyst (50 mg) and glass beads (remaining volume). A solution of aniline (0.10 mol·l^{-1}), styrene (0.15 mol·l^{-1}) and undecane (internal standard) in octane was passed over the catalyst (flow 0.2 ml·min^{-1}). The temperature was increased to 150°C. After steady state was obtained (about 20 min), samples of the product mixture were collected at the end of the reactor for gas chromatography. Subsequently, the temperature was raised every 20 min by 10°C to maximum 300°C. The temperature was then reduced to 150°C and confirmed that the initial activity was obtained.

[†] DPPF = 1,1'-*bis*(diphenylphosphino)ferrocene, EMIm = 1-ethyl-3-methylimidazolium trifluoromethane sulphonate, BMIm = 1-butyl-3-methylimidazolium trifluoromethane sulphonate, HMIm = 1-hexyl-3-methylimidazolium trifluoromethane sulphonate, HM$_2$Im = 1-hexyl-2,3-dimethylimidazolium trifluoromethane sulphonate.

3. Results and Discussion

Analysis of the porosity by nitrogen adsorption showed that the ionic liquid entirely filled pores with less than 9 nm radius, whereas larger pores remained unaffected. However, the entire silica surface was covered by ionic liquid as was shown by IR spectroscopy. The ^{1}H MAS NMR spectra of the materials were surprisingly well resolved and the signal for each proton of the imidazolium cation was identified (Fig. 2). The additional broad signal is assigned to the acidic proton of CF_3SO_3H.
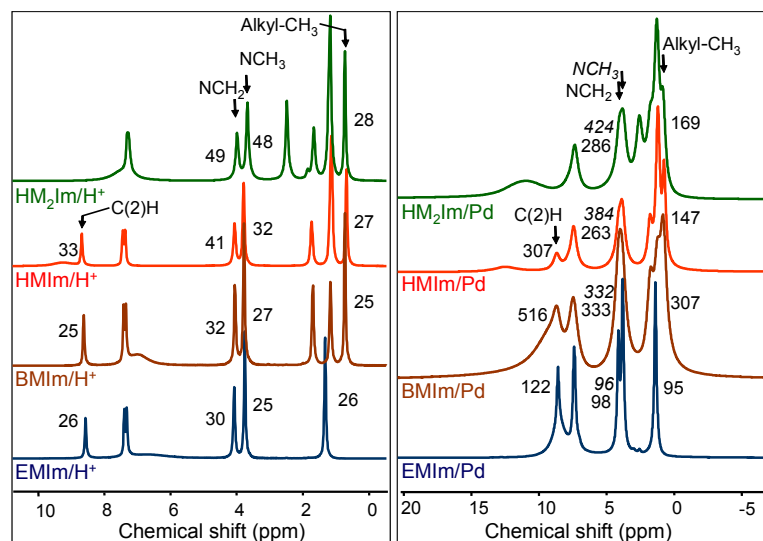
Fig. 2 ^{1}H MAS NMR spectra (298 K) of series $H^+/IL/SiO_2$ (left) and $Pd3/IL/SiO_2$ (right) and line-widths (/Hz) of selected signals.

The line-width of the nitrogen bound methyl and methylene groups increased with increasing size of the imidazolium cation in the order $H^+/EMIm/SiO_2$ < $H^+/BMIm/SiO_2$ < $H^+/HMIm/SiO_2$ < $H^+/HM_2Im/SiO_2$. This shows that the mobility of the aromatic ring decreased with increasing size of the imidazolium cation. On the other hand, the line-width of the terminal methyl group in the alkyl side chain was equal (25-28 Hz) showing that the flexibility of the alkyl group was not influenced by the size of the cation. A large increase of the line-width was observed, when $[Pd(DPPF)(CF_3CO_2)_2]$ and CF_3SO_3H were immobilized in the supported ionic liquids. This suggests a substantial decrease in the mobility of the imidazolium cations.

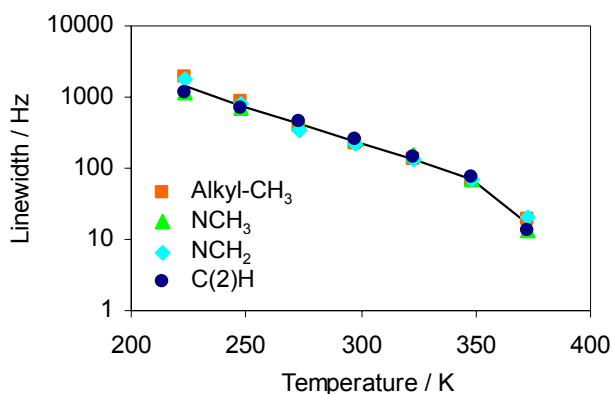**Fig. 3** Temperature dependence of the line-width of selected protons in the ^{1}H MAS NMR spectra of $Pd3/EMIm/SiO_2$.

The dynamic interaction of ionic liquid and Pd complex was investigated by temperature resolved MAS NMR experiments. For all samples, the line-width of all peaks decreased exponentially with temperature. A change of slope in the logarithmic plot indicates that a phase transition from glassy to liquid state occurred at *ca.* 348 K for EMIm/Pd and BMIm/Pd (Fig. 3). For HMIm/Pd, the phase transition occurred above 373 K. After the phase transition the line-width in the spectra of the IL/Pd samples was similar to that of the IL/H$^+$ series at 298 K. To explain these observations we propose that the imidazolium cations form a solvent cage around the palladium complexes, thereby establishing a long range ordered system [7], which in turn is responsible for the reduced mobility (Fig. 4).
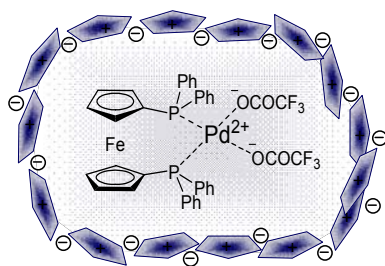

Fig. 4 Artist's impression of the solvent cage of ionic liquid molecules around the palladium complex.

The bi-functional catalysts were tested for their catalytic activity in the addition of aniline to styrene (Eq. 1). In catalytic reaction at 125°C in a batch reactor, the Markownikoff product *N*-(1-phenyl-ethyl)-aniline was formed with a selectivity of 100% over all catalysts (based on aniline conversion). The selectivity based on styrene was lower (50 - 95%), as oligomerisation occurred as side reaction. The catalytic activity of the catalysts increased in the sequence HM$_2$Im < HMIm < BMIm < EMIm. Thus, the IL with higher polarity provided a higher activity. The initial catalytic activity was linearly correlated with the Pd loading, which corresponds to first order in palladium. However, catalytic activity was only observed, when the palladium concentration exceeded $\sim 9 \cdot 10^{-3}$ mmol$_{Pd2+}$·g$_{Cat}^{-1}$. We suggest that for all catalysts an equal amount of the palladium complex was strongly adsorbed to the silica surface and did not participate in the catalytic reaction.

(eq. 1)
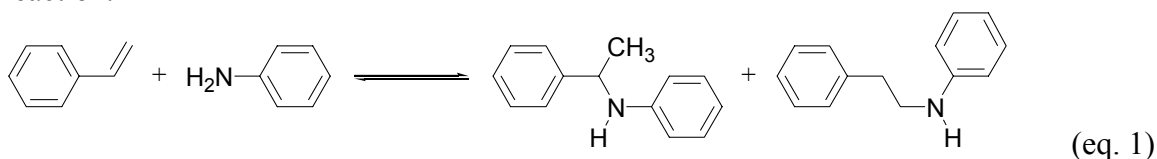
The reaction was studied in further detail at reaction temperatures up to 300°C using a fixed bed reactor (Fig. 5). Conversion of aniline started at 150°C. With increasing temperature, the activity of the catalysts increased exponentially to reach a maximum at ~ 240°C. Steady state conversion of 65% at this temperature (EMIm based catalyst, 0.044 mmol$_{Pd}^{2+}$·g$_{Cat}^{-1}$) corresponds to an integral reaction rate of 8.4 mmol (g$_{Cat}$·h)$^{-1}$ and a turnover frequency of 199 mol·(mol$_{Pd}^{2+}$·h)$^{-1}$. The Markownikoff isomer *N*-(1-phenyl-ethyl)-aniline was formed at lower temperatures, whereas at higher temperatures the corresponding *anti*-Markownikoff isomer *N*-(2-phenyl-ethyl)-aniline was observed, too. At temperatures above 250°C, the conversion decreased as the thermodynamic limit of the (slightly exothermic) reaction was encountered. In the thermodynamic regime, the ratio of the Markownikoff to the *anti*-Markownikoff product was approximately equal for all catalysts (0.77(3), 0.75(1) and 0.65(4) for the EMIm, BMIm and HM$_2$Im based catalyst, respectively) and nearly independent of the temperature.
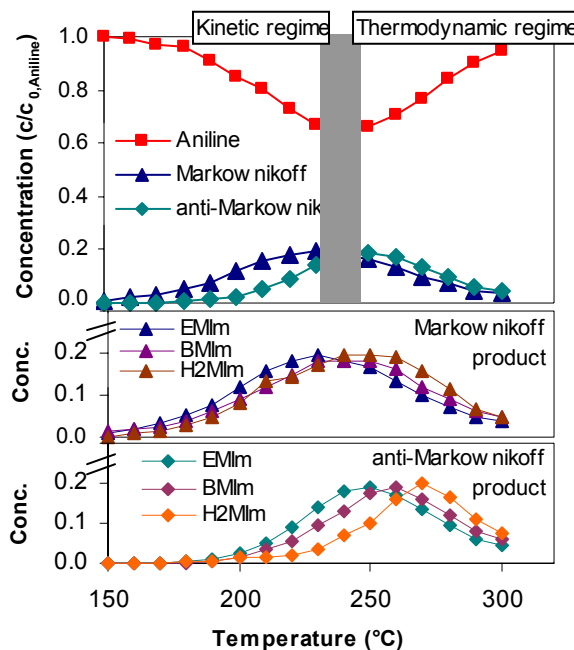
Fig. 5 Temperature dependence of the addition of aniline to styrene with Pd3/EMIm/SiO$_2$ performed in a fixed bed reactor (top) and comparison of the yield in *N*-(1-phenyl-ethyl)-aniline (middle) and *N*-(2-phenyl-ethyl)-aniline (bottom) with catalysts differing in the supported ionic liquid..

Several mechanisms for hydroamination have been discussed in literature [14-18]. Two mechanisms appear most likely for Lewis acidic late transition metal complexes in the presence of a Brønsted acid: nucleophilic attack on a coordinated styrene (path A) and insertion of styrene into a palladium – hydride bond as key step (path B). Based on the observations given above, we suggest that the formation of the Markownikoff product follows the mechanistic path A (Fig. 6). Coordination of styrene to the palladium centre *via* the olefinic π-system renders it susceptible to a nucleophilic attack of the lone electron pair of the aniline nitrogen atom. Formal 1,3-proton shift from the ammonio-group to the α-carbon atom and protolytic cleavage of the metal–carbon bond is rate determining. In the temperature range of stable solvent cages, the more polar ionic liquid is concluded to provide intrinsically higher rate of reaction, which is either related to faster proton transfer within of the solvent cage or stabilisation of a polar transition state associated with the rate determining step [6]. At high temperatures, where the ionic liquid is similar to a classic solvent, the differences between the catalytic activities of the catalysts differing in ionic liquid are less pronounced.
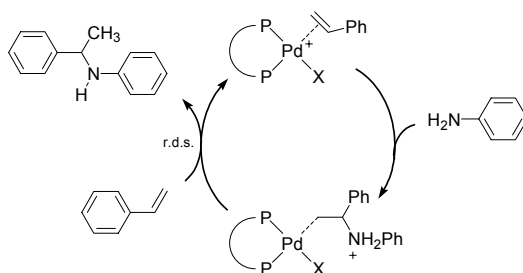

Fig. 6 Mechanism proposed for the formation of the Markownikoff product.

For the formation of the *anti*-Markownikoff product, we suggest mechanistic path B (Fig. 7). During an initial reduction step, a palladium hydride is formed. Subsequently, the olefinic double bond of styrene is inserted into the Pd-H bond. Nucleophilic attack (r.d.s.) of the lone electron pair of the aniline nitrogen atom at the α-carbon atom provides the *anti*-Markownikoff product, which desorbs from the coordination sphere of the palladium centre. It is speculated that the higher aniline concentration in the ionic liquid phase with higher polarity leads to higher turnover frequencies in the r.d.s. In this respect, the absorption constant of aniline from heptane into the supported ionic liquid phase was determined decreasing in the sequence EMIm > BMIm > HM$_2$Im (0.235, 0.221 and 0.204 mmol$^.$g^{-1}, respectively). Only part of the adsorbed aniline was physically dissolved in the supported catalyst phase (0.037, 0.018 and 0 mmol$^.$g^{-1}, respectively), while the remainder was either protonated, or bound to the Pd centre (aniline/Pd = 2/1). In case of mechanistic path B, the product distribution is determined by the regioselectivity of the insertion step. The steric demand of the phenyl group allows only formation of the 2-phenyl-ethyl palladium complex, while strong steric conflicts arise between the phenyl-group of styrene and the phenyl groups at the phosphine during formation of the 1-phenyl-ethyl palladium complex.
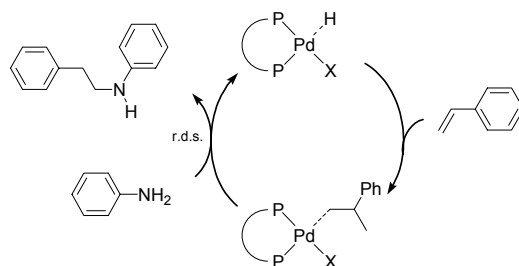

Fig. 7 Mechanism proposed for the formation of the *anti*-Markownikoff product.

4. Conclusions

The present report is the first experimental evidence for the formation of ordered three-dimensional structures in solutions of organometallic complexes in a thin film of supported ionic liquid. The ordering effect leads to a drastically reduced mobility of ionic liquid and complex molecules, and can be used to induce unusual properties in the supported complexes. For the addition of aniline to styrene, the material provided exceptional catalytic activity providing the Markownikoff product under kinetically controlled conditions and also the *anti*-Markownikoff product in the thermodynamic regime. Thus, the concept of to synthesising novel bi-functional catalysts by immobilising a Lewis acidic palladium complex and a strong Brønsted acid in a thin film of supported ionic liquids was proven as fully functional. Possible applications in other reactions include the enhancement of metal-substrate interactions, the re-orientation of substrate molecules within in the solvent cage during a two-step catalytic process, and the possibility of directing the approach of molecules to catalytically active centres.

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