

## **Multi-functional catalysts for process intensification**

Richard T. Knapp, Thomas E. Müller, Johannes A. Lercher

*Department Chemie, Lehrstuhl II für Technische Chemie, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany, Tel. +49 89 28912827, Fax +49 89 28913544, E-Mail: thomas.mueller@tum.de*

### **1. Abstract**

Immobilization of catalytically active organometallic complexes by dissolution in supported films of ionic liquids has recently been introduced as strategy to derive new heterogeneous catalysts. This allows preparing molecular catalysts in a widely tailorable environment without the drawbacks of complex grafting chemistry. This novel class of materials combines the advantages of homogeneous and heterogeneous catalysts. Different functionalities can be joined in a single material. However, the influence of the environment of ionic liquid with high dielectric constant on structure and reactivity of the complexes remains unknown. In this paper, bi-functional catalysts based on supported ionic liquids were explored for various applications, such as hydroamination of alkenes, enantioselective hydrogenation. It is demonstrated that the catalysts combine exceptional activity with custom-tailored selectivity. Detailed characterization provided experimental evidence for the formation of supramolecular structures in solutions of organometallic complexes in the ionic liquid. The ordering effect leads to drastically reduced mobility of ionic liquid and complex molecules, and can be used to induce unusual properties in the supported complexes. The formation of solvent cages occurs also in case of supported metal cluster.

Keywords: Immobilisation, Supported ionic liquid, Heterogeneous catalysis, Bi-functional, Structure-activity relationship

### **2. Introduction**

Ionic liquids are a class of novel solvents with extremely high polarity [1]. Immobilization of organometallic complexes in thin films of supported ionic liquid has been suggested as a novel concept to combine the high selectivity of homogeneous catalysts with the easy separation of a heterogeneous system [2]. The strategy allows fixing molecular catalysts in a widely tailorable environment without the drawbacks of complex grafting chemistry (see Fig. 1).

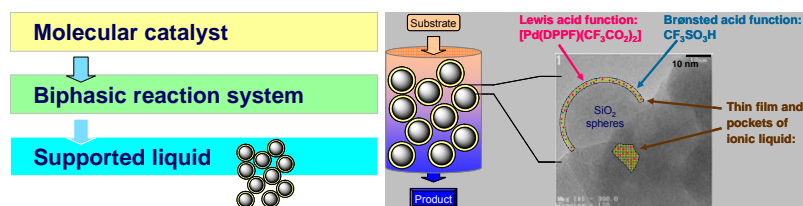


Fig. 1: Concept for immobilization of molecular catalysts and realization for fixed bed applications.

Covering supported metal nanoparticles with ionic liquid, as schematically shown in Fig. 2, may also have many advantages, like preventing the oxidation of the metal and controlling the access of substrate molecules to the metal surface.

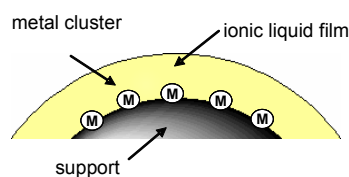


Fig. 2: Concept of metal clusters immobilized in thin films of ionic liquid.

The question arises, however, to what extent the highly polar ionic liquid influences the structure of the metal organic complex, the properties of complexes and metal cluster and *vice versa*, how the ionic liquid is influenced by the presence of complexes and metal nanoparticles. Recently, ordering phenomena and domain formation have been reported [3-4]. In this study, these effects as well as the performance of supported complexes in catalysis of hydroamination and enantioselective hydrogenation reactions were investigated.

### 3. Experimental

#### 3.1. Immobilized palladium complexes

Bi-functional heterogeneous hydroamination catalysts were prepared by immobilisation of both a Brønsted acid and a Lewis acidic palladium complex in silica supported thin films of ionic liquid. Catalytically active metal complexes, additives and ionic liquids were dissolved in dichloromethane. The silica support was added and the solvent removed by freeze-drying to obtain a free flowing powder. Catalysts IL/Pd were prepared with imidazolium salts  $C_3N_2H_2MeRAlkyl^+ CF_3SO_3^-$  ( $R = H, Me$ ; Alkyl =  $C_2H_5, C_4H_9, C_6H_{13}$ ) decreasing in polarity (IL = EMIm, BMIm, HMIm and BDiMIm, respectively). Samples IL/ $H^+$  were prepared in the same way without Pd complex.

#### 3.2. Immobilized metal clusters

As support, Aerolyst 355® (from Degussa GmbH) was grinded, sieved to ca. 100  $\mu m$  particle size and dried at 120 °C. Catalysts with immobilized metal clusters were prepared by incipient wetness impregnation. The metal salts, mostly nitrates, were dissolved in the appropriate amount of bi-distilled water. The solutions were then

trickled onto the support and the mixture was stirred until the water was completely absorbed. These precursors were calcined in synthetic air and subsequently reduced in a flow of hydrogen. Finally, the catalysts were coated with ionic liquids of different polarity.

### 3.3. Catalyst characterisation and catalysis

NMR measurements were performed on a Bruker AV500 spectrometer using magic angle spinning (MAS). The immobilized palladium complexes were tested in the addition of aniline to styrene using a fixed bed reactor operated at 423-573 K.

## 4. Results and discussion

### 4.1. Immobilized organometallic complexes

The interaction of organometallic complexes with ionic liquids was investigated for the test system  $[\text{Pd}(\text{DPPF})(\text{CF}_3\text{CO}_2)_2]$  immobilized in a thin film of 1-ethyl-3-methylimidazolium trifluoromethane sulphonate on silica (EMIm/Pd). Analysis of the porosity by nitrogen adsorption showed that the ionic liquid (IL) entirely filled pores with less than 9 nm radius, whereas larger pores remained unaffected. To analyze the mobility and local structure of the molecules,  $^1\text{H}$  MAS NMR spectra of EMIm/Pd as well as of the parent EMIm and a sample not containing the palladium complex (EMIm/ $\text{H}^+$ ) were recorded (Fig. 3). While the position of the signals assigned to the imidazolium cation of EMIm remained equal, the line width of all resonances increased, when the ionic liquid was immobilized on  $\text{SiO}_2$ . The increase in line width was much more pronounced, when the Pd complex was present in the IL phase.

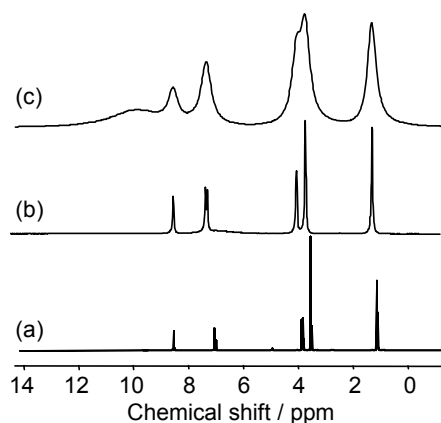


Fig.3:  $^1\text{H}$  MAS NMR spectra of (a) pure EMIm, (b) EMIm/ $\text{H}^+$  and (c) EMIm/Pd.

In order to understand these observations, we have investigated the line broadening effect in further detail. The  $^1\text{H}$  MAS NMR spectra of the samples IL/ $\text{H}^+$  were well resolved and the signal for each proton of the imidazolium cation was identified (Fig. 4). The broad signal with variable position is assigned to the acidic proton of  $\text{CF}_3\text{SO}_3\text{H}$ . The line width of the nitrogen bound methyl and methylene groups in-

creased with increasing size of the imidazolium cation indicating that the mobility of the aromatic ring decreased in this sequence (Fig. 4).

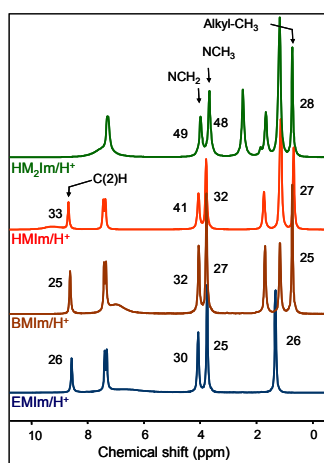


Fig. 4: Solid state  $^1\text{H}$  MAS NMR spectra of supported catalysts  $\text{IL}/\text{H}^+$ . The numbers indicate the line width in Hz.

A large increase of the line width was observed, when  $[\text{Pd}(\text{DPPF})(\text{CF}_3\text{CO}_2)_2]$  and  $\text{CF}_3\text{SO}_3\text{H}$  were immobilized in the supported ionic liquids (Fig. 5). This suggests a substantial decrease in the mobility of the imidazolium cations. 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, which in turn is responsible for the reduced mobility of the ionic liquid ion pairs.

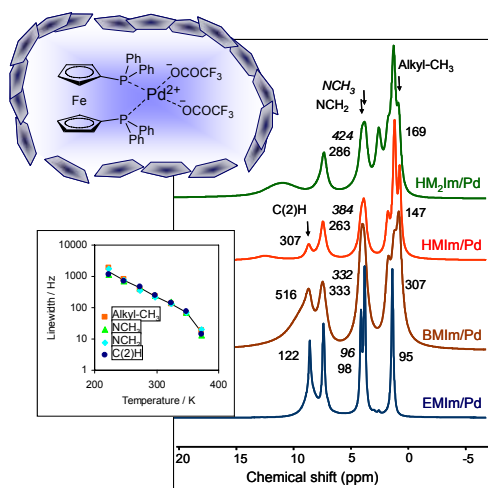
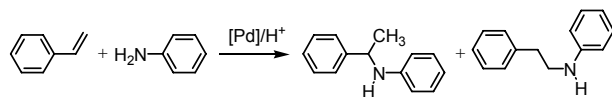


Fig. 5: Solid-state  $^1\text{H}$  MAS NMR spectra of supported catalysts  $\text{IL}/\text{Pd}$  and concept of solvent cages of IL. The numbers indicate the line width in Hz.

The differences in the line width are assigned to a systematic variation in  $T_2$  and can be taken as an indicator for the mobility of the corresponding atomic group [4]. The large increase of the line width upon addition of a complex indicates that supramolecular structures are formed in the ionic liquid phase. We have assigned this effect to the generation of solvent cages (Fig. 5), which are a consequence of disrup-

tion of the inter-ionic interactions induced by the presence of the organometallic complex. In an attempt to minimize the potential energy, the coordination sphere around the complex assumes a minimum size.



Eq. 1

The supported palladium complex EMIm/Pd was tested as catalyst for the hydroamination of styrene with aniline (Eq. 1), which yielded the Markownikoff product *N*-(1-phenylethyl)aniline (**1**) and the *anti*-Markownikoff product *N*-(2-phenylethyl)aniline (**2**) [2]. In the kinetic regime ( $T < 513$  K), product **1** was formed with high selectivity, whereas a preference for **2** was found under thermodynamic control ( $T > 513$  K). In contrast, only the Markownikoff product was obtained at low temperatures in classic solvents, such as toluene. In other words, the chemoselectivity of this system can be tuned by using ionic liquids.

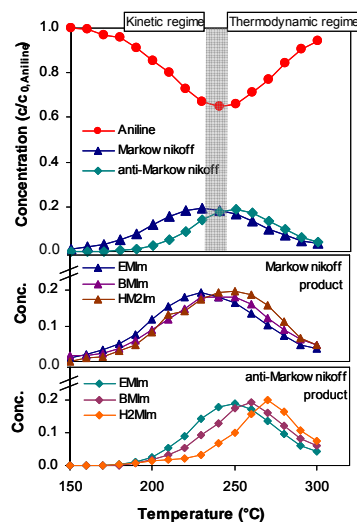


Fig. 6: Catalytic activity of IL/Pd in the addition of aniline to styrene. The concentrations in the product mixture at the exit of the fixed-bed reactor in steady state is shown.

Further, the effect of the solvent cages on enantioselectivity was investigated for the hydrogenation of acetophenone to (*S*)-1-phenylethanol using  $[\text{Rh}((S)\text{-BINAP})\text{-}(\text{COD})]\text{-ClO}_4\text{thf} / \text{K}_2\text{CO}_3$  immobilized in a thin film of phosphonium based ionic liquid on silica. Enantioselectivities up to 74 % were achieved, while only 4 % ee were found for the same catalyst-substrate pair in methanol. We speculate that the superior chiral induction is due to strongly enhanced interactions between catalyst and substrate within of the solvent cages.

#### 4.2. Immobilized metal nanoparticles

IR spectroscopy was used to characterize the surface chemistry. The IR spectrum of an immobilized platinum catalyst in comparison to the supported ionic liquid and the

parent support is shown in Fig. 7. For the parent support, a band at  $3745\text{ cm}^{-1}$  characteristic of silanol groups was observed. The broad band at  $3594\text{ cm}^{-1}$  is assigned to internal hydrogen bonded hydroxyl groups. Upon adsorption of the ionic liquid, the band corresponding to terminal SiOH groups disappeared, while a new broad band appeared at  $3320\text{ cm}^{-1}$ . This indicates that all silanol groups interact with the ionic liquid *via* hydrogen bonds. Thus, we conclude that the entire silica surface is covered by the ionic liquid.

The IR spectra of the supported catalysts showed several bands corresponding to the ionic liquids at  $2700\text{--}3300\text{ cm}^{-1}$  (asymmetric and symmetric stretching vibrations of  $\text{CH}_3$  and  $\text{CH}_2$  groups),  $1700\text{--}1600\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  stretching vibration) and  $1500\text{--}1300\text{ cm}^{-1}$  ( $\text{CH}$  bending vibrations).

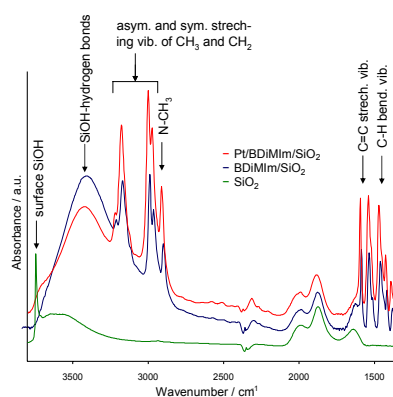


Fig. 7: IR spectra of the support, the supported ionic liquid and of a supported Pt cluster.

The synthesized catalysts were also characterized by transmission electron microscopy, to determine the particle size of the metal clusters. A TEM picture of a sample with Pt clusters suspended in an ionic liquid and supported on silica is shown in Fig. 8. The mean metal particle size of the clusters was in the range of 2.0 nm. The picture clearly illustrates that the particles were highly dispersed and that there were no agglomerates of the metal clusters.

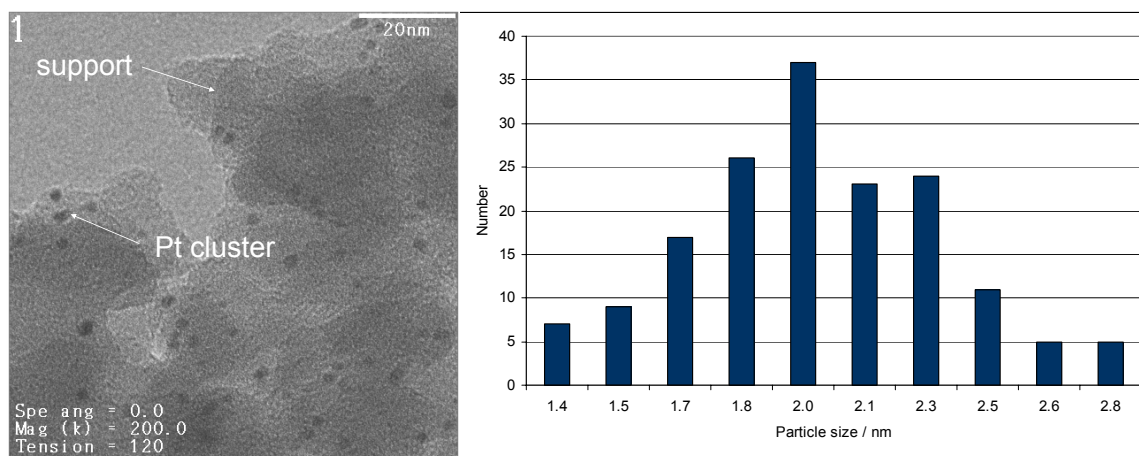


Fig. 8: TEM picture of a Pt-catalyst at a magnification of 1:200.000 (left) and particle size distribution (right).

To determine the electronic structure of the metal clusters, the catalysts were analyzed with EXAFS and XANES. The measured and calculated Fourier-transformed EXAFS spectra of a palladium catalyst that was prepared with a time gap between reduction and coating of ten days shows a considerable contribution of Pd-O (Fig. 9, left). After activation in H<sub>2</sub> (20 mL/min) at 170 °C, the Pd-O contribution vanished (Fig. 9, right).

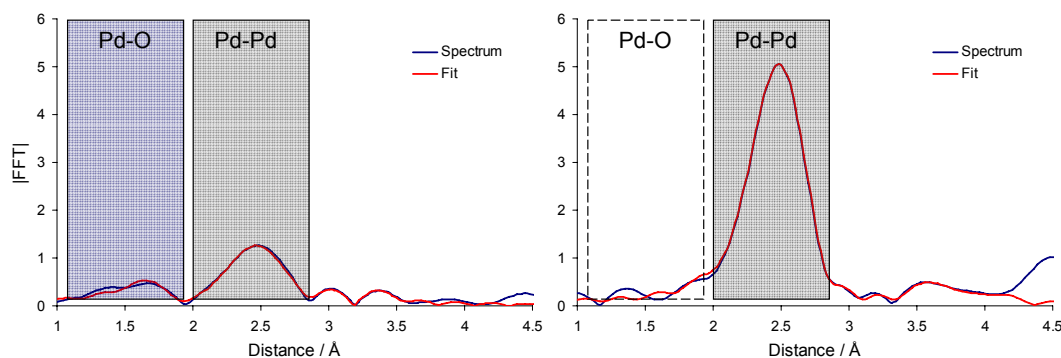


Fig. 9: Measured and calculated Fourier-transformed EXAFS spectra of a Pd catalyst before (left) and after (right) activation in 20 mL/min H<sub>2</sub> at 170 °C.

The results of the calculated EXAFS spectra are shown in Tab. 1. Clearly, the palladium is oxidized before activation. After activation, the spectrum can only be fitted assuming that no oxygen atoms are in vicinity.

Tab. 1: Atomic distances and number of neighbours as calculated from simulation of the EXAFS spectra

	Before activation	After activation
$r_{\text{Pd-O}}$	2,07 Å	---
$N_{\text{O}}$	1,6	---
$r_{\text{Pd-Pd}}$	2,73 Å	2,75 Å
$N_{\text{Pd}}$	4,4	10,1

The change in the electronic structure of palladium can also be followed by XANES. The spectrum of the palladium catalyst before activation has significant differences to the reference foil of metallic palladium (Fig. 10), whereas the activated catalyst looks nearly identical to the reference.

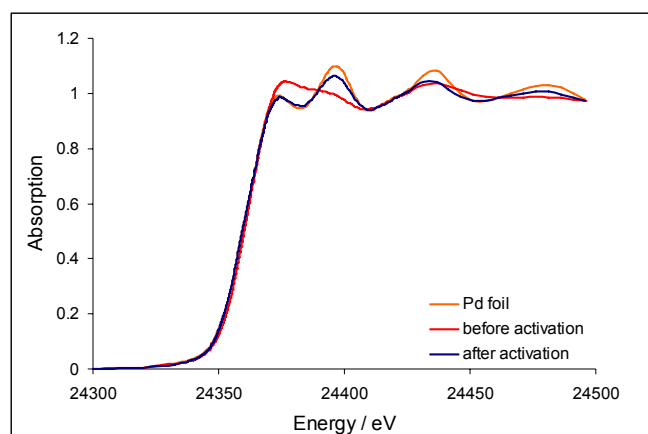


Fig. 10: XANES Spectra of a Pd-catalyst before and after activation with 20 mL/min H<sub>2</sub> at 170 °C compared to a palladium reference foil.

To prove that immediate impregnation with ionic liquid prevents oxidation of the metal, catalysts were analyzed, where the metal clusters were covered with ionic liquid directly after the reducing step (Fig. 11). Even easily oxidisable metals like copper can be kept at the oxidation state of zero if the ionic liquid is applied instantly.

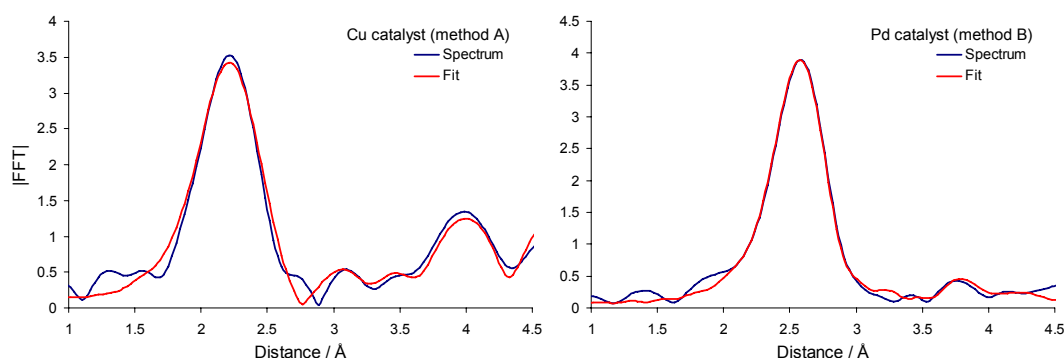


Fig. 11: Measured and calculated Fourier-transformed EXAFS spectra of a copper catalyst (left) and a platinum catalyst (right).

## 5. Conclusions

The present study provides clear evidence for the formation of three-dimensional solvent cages of ionic liquid molecules around organometallic complexes and metal clusters providing a reaction environment, which distinctly differs from classic solvents.

Immobilized complexes showed exceptional catalytic activity for the addition of aniline to styrene providing the Markownikoff product under kinetically controlled conditions. In the thermodynamic regime at higher temperatures, also the *anti*-Markownikoff product was obtained. In case of the Markownikoff product, the more polar ionic liquid provided intrinsically higher rate of reaction, which is related to stabilisation of a polar transition state associated with the rate determining step (Fig.6). In case of the *anti*-Markownikoff product, the higher aniline concentration in the



ionic liquid phase with higher polarity is speculated to lead to higher turnover frequencies in the rate-determining step.

By appropriate choice of the metal clusters and by using ionic liquids as surface mediators, the properties of the supported metal catalysts can also be fine-tuned. In particular, solubility and, thus, selectivity for different reactants can be adjusted by selecting the polarity of the ionic liquid. The activity of catalysts characterised with the different methods mentioned above will be compared for various catalytic applications.

The results may open new synthetic pathways, in particular for chemo- and stereoselective reactions. The concept of supported catalysts has been proven as straightforward method to derive heterogeneous from homogeneous catalysts.

## 6. References

- [1] Welton, T., (2004) *Coord. Chem. Rev.*, 248, 2459 – 2477.
- [2] Jimenez, O.; Müller, T. E.; Sievers, C.; Spirkel, A. and Lercher, J. A., (2006) *Chem. Commun.*, 28, 2974 – 2976.
- [3] Atkin, R. and Warr, G. G., (2005) *J. Am. Chem. Soc.*, 127, 11940 – 11941.
- [4] Sievers, C.; Jimenez, O.; Müller, T. E.; Steuernagel, S. and Lercher, J. A., (2006) *J. Am. Chem. Soc.*, 128, 13990 – 13991.