

Solvent cages of ionic liquid: structure and effect on catalysis

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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 recently been suggested as a novel concept to combine the high selectivity of homogeneous catalysts with the easy separation of a heterogeneous system [2]. First catalytic studies show a high potential of these systems [3]. Ordering phenomena and domain formation have been reported in recent studies [4-6]. Here, the formation of solvent cages around supported organometallic complexes is demonstrated by NMR spectroscopy. The effect on catalytic reactions is discussed.

Materials and Methods

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. NMR measurements were performed on a Bruker AV500 spectrometer using magic angle spinning. The materials were tested in the addition of aniline to styrene (fixed bed reactor, 423-573 K) and the hydrogenation of acetophenone (slurry phase, 323 K).

Results and Discussion

The interaction of supported ionic liquids with organometallic complexes was investigated using $[\text{Pd}(\text{DPPF})(\text{CF}_3\text{CO}_2)_2]$ immobilized in a thin film of 1-ethyl-3-methyl-imidazolium trifluoromethane sulphonate on silica (Pd/EMIM/SiO₂) as test system. Analysis of the porosity by nitrogen adsorption showed a decrease of the mesopore volume from 0.76 cm³ g⁻¹ (silica support) to ca. 0.13 cm³ g⁻¹ (supported catalysts). Closer inspection of the isotherm showed that the ionic liquid entirely filled pores with less than 9 nm radius, whereas larger pores remained unaffected. The ¹H MAS NMR spectra of pure EMIM as well as EMIM/SiO₂ and Pd/EMIM/SiO₂ are shown in Figure 1. The line width of all resonances increased when the ionic liquid was immobilized on SiO₂. The increase was much more pronounced when the complex was present in the IL phase. This difference in the line widths is due to a difference in T₂ and can be taken as an indicator for the mobility of the corresponding atomic group [6]. The large increase of the line width upon addition of a complex indicates that supramolecular structures are formed in the ionic liquid (Figure 2). We have assigned this to the generation of solvent cages, which are a consequence of disruption 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.

Pd/EMIM/SiO₂ was tested as catalyst for the hydroamination of styrene with aniline, which yields *N*-(1-phenylethyl)aniline (**1**) as Markownikoff product and *N*-(2-phenylethyl)aniline (**2**) as *anti*-Markownikoff product [3]. In the kinetic regime (T ≤ 513 K),

product **1** was formed with high selectivity, whereas a preference for **2** was found under thermodynamic control. In other words, the chemoselectivity of this system can be tuned over a wide range.

Further, the effect of the solvent cages on the enantioselectivity was investigated for the hydrogenation of acetophenone to (*S*)-1-phenylethanol using $[\text{Rh}((S)\text{-BINAP})(\text{COD})]\text{ClO}_4^-$ thf / K₂CO₃ immobilized in a thin film of phosphonium based ionic liquid on silica [7]. Enantioselectivities up to 74 % were achieved, while only 4 % ee were reported for the same catalyst-substrate pair in methanol [8]. We speculate that the chiral induction is superior within of the solvent cages due to strongly enhanced interactions between catalyst and substrate.

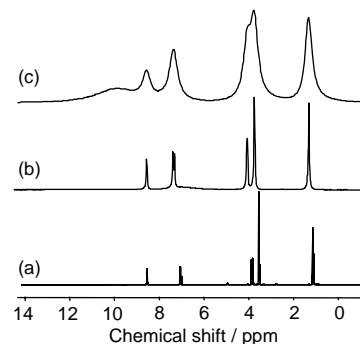


Figure 1. ¹H MAS NMR spectra of (a) pure EMIM, (b) EMIM/SiO₂ and (c) Pd/EMIM/SiO₂

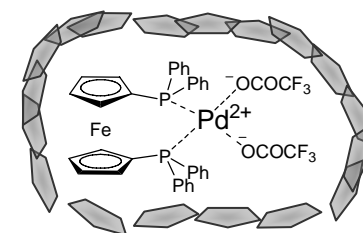


Figure 2. Schematic drawing of the solvent cages of imidazolium based ILs around a $[\text{Pd}(\text{DPPF})(\text{CF}_3\text{CO}_2)_2]$ complex.

Significance

The present study provides clear evidence for the formation of three-dimensional solvent cages of ionic liquid molecules around organometallic complexes. First catalytic investigations indicate that this phenomenon provides a reaction environment, which distinctly differs from classic solvents. The results provide an improved understanding of ionic liquids as reaction medium and may open new synthetic pathways, in particular for stereoselective reactions.

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