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Markownikoff and *anti*-Markownikoff hydroamination with palladium catalysts immobilized in thin films of silica supported ionic liquids†

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The concept of immobilising organometallic complexes in a thin film of supported ionic liquids was utilised to synthesise novel bi-functional catalysts combining soft Lewis acidic and strong Brønsted acidic functions; the materials showed exceptional catalytic activity for the addition of aniline to styrene, providing the Markownikoff product under kinetically controlled conditions and mainly the *anti*-Markownikoff product in the thermodynamic regime.

The direct addition of amines to weakly or non-activated alkenes (hydroamination) is an important target reaction. For industrial applications, however, the known catalysts provide insufficient activity and long-term stability. Thus, a new generation of—preferentially solid—catalysts is required. Bi-functional catalysts combining soft Lewis acidic function (activation of the alkene) and strong Brønsted acidic function (acceleration of the rate determining step (r.d.s.)) were reported to provide high catalytic activities.[1] A new concept, immobilisation of homogeneous catalysts in a supported film of ionic liquid,[2] allows joining both functions in one material and tailoring systematically its performance in catalysis.

As Lewis acid function, the palladium complex [Pd(DPPF)(CF₃CO₂)₂], prepared *in-situ* from Pd(CF₃CO₂)₂ and 1,1′-bis(diphenylphosphino)ferrocene (DPPF), was chosen. Trifluoromethanesulfonic acid (TfOH) provided the Brønsted acid function. Complex and acid ($Pd^{2+}/H^+ = 1/10$) were immobilised in a thin film of imidazolium based ionic liquids‡ on a silica support (Fig. 1).† Systematic increase in the length of the alkyl chain provided a series of catalysts with decreasing polarity of the ionic liquid phase.
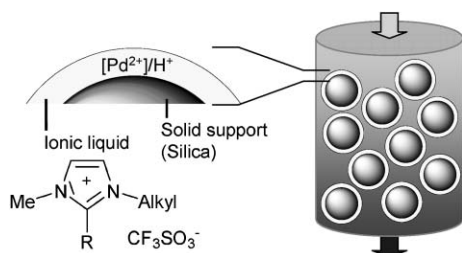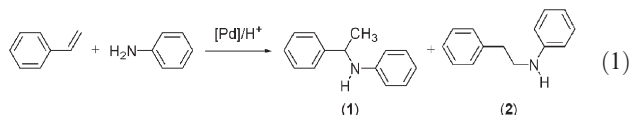
As test reaction, the addition of aniline to styrene was investigated (Eq. 1). The reaction can, in principle, provide the Markownikoff product *N*-(1-phenylethyl)aniline (**1**) and the *anti*-Markownikoff product *N*-(2-phenylethyl)aniline (**2**).

$$(1)$$

In batch experiments performed at low temperatures (125 °C), the Markownikoff addition product **1** was the only product apart from some oligomerization products of styrene. The initial catalytic activity increased linearly with the Pd loading (Fig. 2) corresponding to first order in Pd complex. However, a minimum loading of 0.011 $mmol_{Pd^{2+}}\ g_{Cat}^{-1}$ seemed necessary and no conversion was observed at lower loadings or without palladium.§ This suggests that, in each case, an equal amount of the Pd complex was irreversibly adsorbed on the silica surface and did not contribute to the catalytic activity.

Particularly noteworthy is that the initial catalytic activity was strongly dependent on the choice of the ionic liquid. The highest catalytic activity was observed for the EMIm‡ based catalyst (1.47 mmol $(g_{Cat}\ h)^{-1}$ at a Pd loading of 0.044 $mmol_{Pd^{2+}}\ g_{Cat}^{-1}$, corresponding to a turnover frequency of 24 mol $(mol_{Pd^{2+}}\ h)^{-1})$, whereas BMIm‡ and HM₂Im‡ provided lower catalytic activities (0.89 and 0.43 mmol $(g_{Cat}\ h)^{-1}$, respectively).

Thus, the highly polar environment of the EMIm containing catalyst is concluded to be particularly favourable. This is attributed to the higher solubility of the reactants in EMIm as the catalyst phase, or to an intrinsically higher rate of reaction in the more polar ionic liquid.
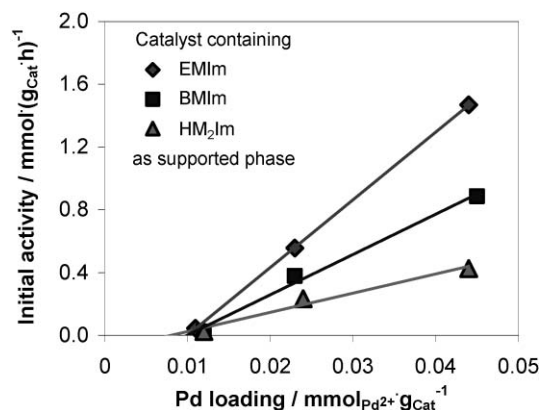
Fig. 1 Concept for the immobilisation of homogeneous catalysts for application in fixed reactors, R = H, Me; Alkyl = C₂H₅, C₄H₉, C₆H₁₃.

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Fig. 2 Catalytic activity of the Lewis/Brønsted bi-functional catalysts in the addition of aniline to styrene (slurry phase, 125 °C).

The absorption constant of aniline from heptane into the supported ionic liquid phase decreased slightly in the sequence EMIm > BMIm > HM$_2$Im (0.235, 0.221 and 0.204 mmol g^{-1}, respectively). Only part of the absorbed aniline was physically dissolved in the supported ionic liquid (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 contrast, no significant absorption of styrene was measured. However, it was reported that co-absorption of aniline and styrene leads to enhanced styrene uptake.[3]

The temperature dependence of the catalytic activity was explored in a fixed bed reactor (Fig. 3). Above 150 °C, the conversion increased exponentially with temperature, attaining a maximum of 35% (EMIm based catalyst, 0.044 mmol$_{Pd^{2+}}$ g$_{Cat}$$^{-1}$) at approximately 240 °C (kinetic regime). At temperatures higher than 240 °C, the conversion decreased as the thermodynamic limit of the (slightly exothermic) reaction was encountered. In the kinetic regime, the main product was **1**, while significant amounts of **2** were formed under thermodynamic control. In the thermodynamic regime, the ratio of products **1** to **2** was approximately equal for all catalysts (0.77(3) : 1, 0.75(1) : 1 and 0.65(4) : 1 for the EMIm, BMIm and HM$_2$Im based catalysts, respectively) and nearly independent of the temperature. Assuming activity coefficients close to one, the difference in thermodynamic stability of the two products was calculated to $\Delta_r G^\circ \approx 1.4(4)$ kJ mol^{-1} (**2** being the more stable product).
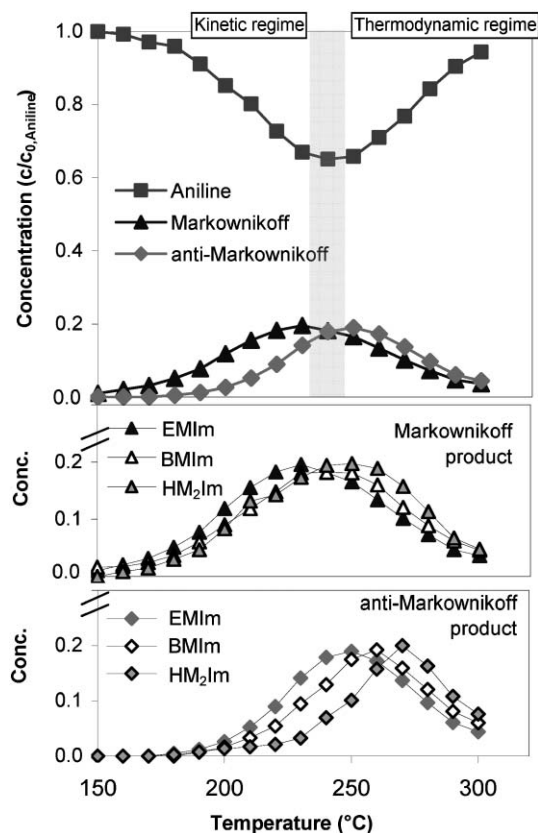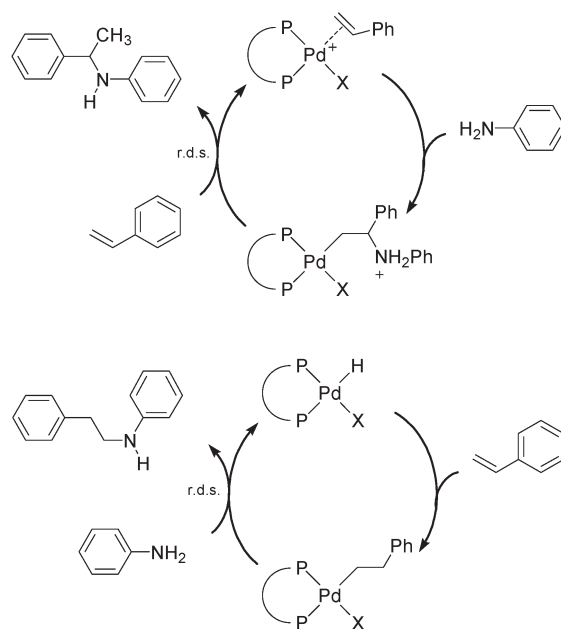

Fig. 3 Temperature dependence with EMIm based catalyst (fixed bed reactor, 0.044 mmol$_{Pd^{2+}}$ g$_{Cat}$$^{-1}$, top) and comparison of the yield in **1** (middle) and **2** (bottom) with catalysts differing in the supported ionic liquid.

In the kinetic regime, the selectivity to **1** was 100% at ≤ 170 °C (for all catalysts) and decreased steadily at higher temperatures. Interestingly, the relative product concentration was strongly dependent on the choice of the ionic liquid. At 220 °C, *e.g.*, the selectivity to **1** was 67, 73 and 87% for the EMIm, BMIm and HM$_2$Im based catalysts, respectively.

The activity of the three catalyst series for formation of **1** was similar in the kinetic regime, decreasing slightly in the sequence EMIm > BMIm > HM$_2$Im. In contrast, for formation of **2** the EMIm based catalyst was 1.7 (4.3) times more active than the BMIm (HM$_2$Im) based catalyst (220 °C). Steady state conversion of 65% (EMIm based catalyst, 0.044 mmol$_{Pd^{2+}}$ g$_{Cat}$$^{-1}$, 240 °C) corresponds to an integral reaction rate of 8.4 mmol (g$_{Cat}$ h)$^{-1}$ and a turnover frequency of 199 mol (mol$_{Pd^{2+}}$ h)$^{-1}$.

Based on the observations given above, and considering the current literature on hydroamination,[4,5] we conclude that two different mechanisms are operative (Scheme 1). The Markownikoff product **1** is probably formed *via* coordination of the olefinic π-system of styrene to the palladium centre, which renders it susceptible to a nucleophilic attack of the lone electron pair of the aniline nitrogen atom.[4] Subsequent protolytic cleavage of the metal–carbon bond is rate determining. The formation of the *anti*-Markownikoff product **2** occurs *via* intermediate formation of a palladium hydride, insertion of the olefinic double bond of styrene and nucleophilic attack (r.d.s.) of the lone electron pair of the aniline nitrogen atom at the α-carbon atom.[5]

In the case of the Markownikoff product, the more polar ionic liquid is concluded to provide an intrinsically higher rate of reaction, which is related to stabilisation of a polar transition state associated with the rate determining step.[6] In the 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.

Scheme 1 Mechanisms proposed for the formation of **1** (top) and **2** (bottom), X = CF$_3$SO$_3$$^-$, CF$_3CO_2$$^-$, r.d.s. = rate determining step.

Notes and references

‡ EMIm = 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, BMIm = 1-butyl-3-methylimidazolium trifluoromethanesulfonate, HM₂Im = 1-hexyl-2,3-dimethylimidazolium trifluoromethanesulfonate.

§ The amount of palladium leached into the reaction solution was below the detection limit of AAS. No further reaction was observed when the filtered reaction mixture was maintained at 125 °C.

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4 See, *e.g.*, H. M. Senn, P. E. Blöchl and A. Togni, *J. Am. Chem. Soc.*, 2000, **122**, 4098.

5 See, *e.g.*, U. Nettekoven and J. F. Hartwig, *J. Am. Chem. Soc.*, 2002, **124**, 1166.

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