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Amine-modified polyionic liquid supports enhance the efficacy of PdNPs for the catalytic hydrogenation of CO_2 to formate†

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Palladium nanoparticles stabilised by aniline modified polymer immobilised ionic liquid is a remarkably active catalyst for the hydrogenation of CO_2 to formate; the initial TOF of 500 h^{-1} is markedly higher than either unmodified catalyst or its benzylamine and *N,N*-dimethylaniline modified counterparts and is among the highest to be reported for a PdNP-based catalyst.

The global demand for a circular economy has led to the exploration of carbon dioxide (CO_2) utilisation to produce value added chemicals such as fuels and feedstocks. Amongst these CO_2-derived commodities, formic acid has been highlighted as a future energy carrier, either acting as a hydrogen storage medium,[1] or *via* direct use in formic acid fuel cells.[2] However, formic acid production currently depends on the hydrolysis of methyl formate, itself obtained from the carbonylation of methanol; while this process is costly and energy intensive, direct hydrogenation of CO_2 to formic acid is attractive as it is single step, and can be achieved under mild conditions with the appropriate catalyst.

While Au[3,4] and Ru[5–7] metal nanoparticles (NP) have been reported to catalyse the hydrogenation of CO_2 to formic acid/formate, studies have been dominated by catalysts based on monometallic[8–12] and bimetallic[13–15] Pd nanoparticles. While a range of supports have been shown to stabilise PdNPs for the hydrogenation of CO_2,[9–16] functionalisation of the support surface with a weakly basic amine has recently been reported to enhance catalytic activity.[3] For example, an improvement in

the performance of PdNPs and PdAgNPs supported on amine-grafted mesoporous carbon or SBA-15, compared with their unmodified counterparts, was attributed to several factors including; (i) the growth of small well-dispersed NPs, (ii) the formation of electron-rich Pd species resulting from charge transfer from silver, (iii) a cooperative role in facilitating the elementary steps of the catalytic cycle and (iv) increasing the CO_2 adsorption capacity/adsorption rate and concentrating the CO_2 around the active site.[16]

The incorporation of ionic liquids (ILs) is an obvious choice in the design of catalysts for CO_2 hydrogenation,[17a] as they are not only effective at stabilizing metal nanoparticles, but they sequester CO_2 and are being explored for applications in carbon capture and storage.[17b] In addition to their role as solvent and sorbent to solubilise CO_2,[6] ILs have been reported to activate CO_2 and stabilise charged intermediates,[8,18] as well as maintain good dispersion of the NPs and prevent aggregation,[5] while basic ILs have been used as buffering media to shift the equilibrium towards free formic acid or formate.[19–21] Polymer immobilized ionic liquids (PIILs) also have attractive credentials as supports for metal nanoparticles as they facilitate recovery of both the metal and the support, enhance catalyst longevity and their CO_2 sorption capacity and sorption/desorption kinetics exceeds their IL counterparts.[22] Moreover, the modular construction of PIILs should improve designability and enable catalysts with improved performance profiles to be developed by modifying the ionic microenvironment, varying the concentration and type of surface organic nitrogen donor, tailoring the structural integrity and porosity and controlling the metal stoichiometry for the synthesis of bimetallic NPs.[23]

Herein, we report the first example of amine-decorated polymer immobilised ionic liquid stabilised PdNPs as catalysts for the hydrogenation of CO_2 to formate. Preliminary studies to explore the efficacy of the catalyst as a function of the composition of the support revealed that the performance depends on the type of amine and its loading and that the highest turnover frequency (TOF, measured as $mol_{formate}\ mol_{Pd}^{-1}\ h^{-1}$) of 500 h^{-1}, obtained

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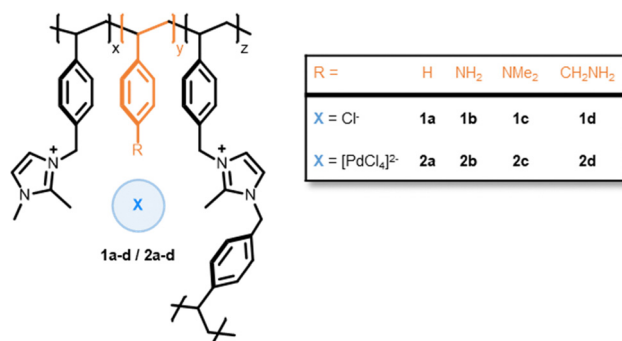
Fig. 1 Composition of amine decorated PIIL supports **1a–d** $[PdCl_4]^{2-}$ loaded precatalysts **2a–d**. Polymers contain 5 mol% cross-linker where x = 0.91, y = 1, z = 0.09.

with PdNPs stabilised by aniline decorated PIIL, is among the highest to be reported.

The first series of amine functionalized PIIL supports **1a–d** were based on a 1,2-dimethylimidazolium monomer, an imidazolium based cross-linker, and an amine modified styrene monomer, with an overall imidazolium to amine ratio of 1 : 1 (Fig. 1). Polymers **1a–d** were impregnated with tetrachloropalladate to afford precatalysts **2a–d**. The solid-state ^{13}C CP-MAS NMR spectra of **2a–d** were similar to those for **1a–d** with the exception of the resonances assigned to the *ipso* N–C atom of the aniline which appeared to shift 30 ppm to lower field, from δ 115 ppm in **1a** to δ 139 ppm in **2a**.

Hydrogenations were conducted in a HEL DigiCAT high pressure reactor, charged with aqueous base (20 mL, 0.65 M), 6 μmol Pd in the form of supported $[PdCl_4]^{2-}$ precatalyst and a total pressure of 40 bar (H$_2$: CO$_2$ = 1:1) at 373 K for 2 h. Formate formation was quantified by ^{1}H NMR spectroscopy, using dimethylsulfoxide as an internal standard.[24] As the precatalysts were reduced *in situ*, under the conditions of catalysis, the corresponding PdNPs were isolated after use for the aqueous phase hydrogenation of CO$_2$ and analysed by HRTEM and HAADF-STEM EDX and shown to be ultrafine and near monodisperse with average diameters between 1.87–3.7 ± 0.4–0.9 nm (Fig. 2 and ESI†). A survey of the activity as a function

of the base, using unmodified precatalyst **2a**, revealed that reactions conducted in the presence of K$_2$CO$_3$ gave a higher TOF than those with KHCO$_3$, NaOH, NEt$_3$ or KOH (Fig. S2a, ESI†), and as such further optimisation of the reaction parameters was performed in 0.65 M aqueous K$_2$CO$_3$. As there have been several other reports that the initial TOF for the hydrogenation of CO$_2$ to formate depends on the base, future studies will investigate whether the type and amount of base affects the size and/or morphology of the NPs, and thereby the activity, or whether the base is involved in the fundamental steps of the catalysis. A study of the influence of the stirring speed and total CO$_2$/H$_2$ pressure on catalyst efficacy was then undertaken to minimise the effect of diffusion. The TOF increased with increasing stirring speed and reached an optimum at 750 rpm (Fig. S2c, ESI†). The TOF also increased from 56 h^{-1} at 10 bar of 1:1 CO$_2$:H$_2$ to an optimum of 166 h^{-1} at 40 bar and then decreased to 138 h^{-1} when the pressure was increased further to 70 bar (Fig. S2b, ESI†). In addition, the TOF decreased with decreasing reaction temperature below 100 °C and also decreased when the reaction temperature was raised to 120 °C (Fig. S2d, ESI†). Comparison of catalyst performance as a function of the amine-modified support against unmodified catalyst revealed that catalyst stabilised by PIIL modified with weakly basic aniline *i.e.* generated from pre-catalyst **2b**, gave a dramatic enhancement in efficacy to afford a TOF of 340 h^{-1}, compared with 166 h^{-1} for catalyst generated from **2a** (Fig. 3a). While support modified with benzylamine (**2d**) also showed a positive effect on catalyst performance, with a TOF of 214 h^{-1}, the use of *N,N*-dimethylaniline modified pre-catalyst **2c** gave a TOF of 130 h^{-1}, slightly lower than the 166 h^{-1} obtained with its unmodified counterpart **2a**. Thus, while primary amines enhance catalyst performance a weakly basic amine is most effective, and a tertiary amine has a negligible impact on the efficacy. Yamashita and co-workers have also reported a similar affect as PdAgNPs supported by *N,N*-dimethylpropylamine modified SBA-15 was slightly less active than unmodified catalyst, for the same reaction, whereas aniline modified SBA-15 showed a large positive effect.[16] The TOF's used herein to compare the efficacy of each
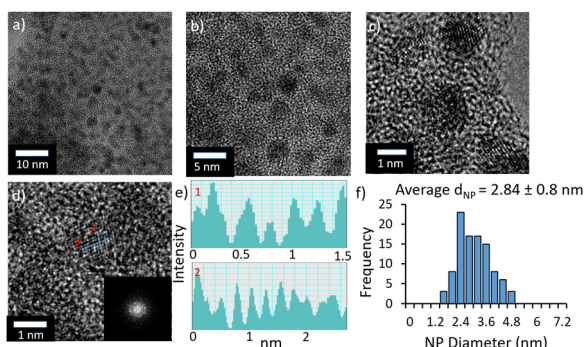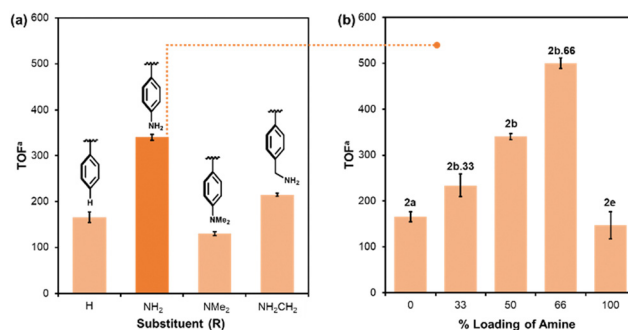

Fig. 2 (a)–(d) High resolution TEM images of PdNPs generated from **2b.66**, with FFT inset (e), line profiles from the HRTEM image (f) and the corresponding size distribution determined by counting >100 particles. Scale bars are 10–1 nm.

Fig. 3 (a) Plot showing TOF against polymer substituent for the thermal hydrogenation of CO$_2$ to formate using PdCl$_4$@PIIL precatalysts **2a–d**. All polymer supports have an IL : co-monomer ratio of 1 : 1. (b) Plot of TOF against mol% loading of amine for catalysts generated from PdCl$_4$@xNH$_2$PIIL (where x = mol% loading of amine). ^{a}TOF = mol$_{formate}$ mol$_{Pd}$$^{-1}$ h^{-1}.

catalyst were determined after a reaction time of 2 h, based on a study of the kinetics of hydrogenation in the early stages of the reaction using precatalyst **2a** and amine-decorated precatalyst **2b.66** (*vide infra*) which showed that there was no observable induction period under the conditions of catalysis (Fig. S3, ESI†).

A study of the influence of increasing the amount of aniline on the support on catalyst efficacy was undertaken by preparing precatalysts stabilised by polymers with 4-aminostyrene and imidazolium monomer ratios of 1:2 and 2:1 as well as poly-4-aminostyrene (**1e**), which, together with **2a** and **2b**, form a series of precatalysts, PdCl$_4$@xNH$_2$PIIL, where x corresponds to the % loading of aniline (x = 0 (**2a**), 33 (**2b.33**), 50 (**2b**), 66 (**2b.66**) and 100 (**2e**)). Interestingly, an almost linear increase in activity was observed with increasing loading of aniline, reaching a maximum TOF of 500 h^{-1} with a TON of 1609 after 14 h for catalyst generated from **2b.66** (Fig. S3, ESI†), which is among the highest to be reported for a monometallic PdNP-based system. Gratifyingly, this TON is also higher than that of 839 and 874 obtained with PdAgNPs supported on phenylamine functionalised SBA-15[16] or mesoporous carbon,[14] respectively, and thus, future studies will target surface modified multi-metallic catalysts with well-defined compositions and explore their efficacy as a function of the metals, their ratio, and the surface functionality. A TOF of 147 h^{-1} was obtained for catalyst supported by the homopolymer of 4-aminostyrene (**1e**), indicating a positive influence of the ionic liquid on catalyst efficacy as amine alone is not sufficient to achieve high activity. Interestingly, a much lower loading of Pd was obtained for 4-aminostyrene homopolymer, **1e** (3.8 wt% compared to an average of 10.9 wt% for the remaining PIIL systems); this may be due to the absence of chloride anions which facilitate impregnation with the tetrachloropalladate *via* ion exchange.

Modification of the support by covalent attachment of the aniline was crucial to achieve high activity as a hydrogenation conducted with catalyst generated from **2a** in the presence of the equivalent amount of aniline as that on the support in **2b.66** resulted in a slight decrease in the TOF to 116 h^{-1}, compared with 146 h^{-1} obtained with **2a**; moreover, the TOF decreased to 92 h^{-1} when the amount of aniline was increased further by 10-fold. Reassuringly, all catalysts described here were more active than commercial Pd/C (10 wt%, Sigma Aldrich), which gave an initial TOF of only 74 h^{-1} under the conditions identified above. In addition, pre-treatment of 6 μmol of Pd/C with a homogeneous solution of **1b.66** (12 μmol) for 16 h prior to performing a hydrogenation did not have a noticeable effect on the activity as the TOF of 51 h^{-1} was only marginally greater than that of 43 h^{-1} obtained with the same loading of Pd/C, but in the absence of **1b.66**.

The possible coordination of amine to Pd in precatalysts **2b–d** was explored by analysing the core-electron excitations of N and Pd using XPS. Charge neutralisation was used for all samples and no rescaling has been applied to quoted binding energies (BEs). Due to the limitations of using advantageous carbon as ref. 25 peak assignment was based on the characteristic BE separation between the elements. First, examination of the local N environment of polymer **1b.66** revealed two peaks at
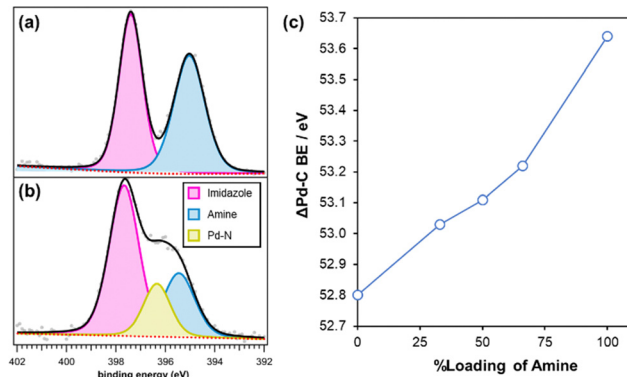

Fig. 4 N 1s XPS spectra of (a) polymer **1b.66** and (b) precatalyst **2b.66**. (c) Plot of BE difference between the Pd 3d$_{5/2}$ and the aliphatic C 1s core electrons against the mol% loading of amine on the precatalyst support.

397.4 eV and 395.0 eV characteristic of nitrogen in the imidazolium and the amine chemical environments, respectively (Fig. 4a). Following impregnation with [PdCl$_4$]$^{2-}$, the imidazolium N 1s peak did not appear to shift significantly for all samples reported in this study (397.5 ± 0.1 eV). The separation in the BE scale of this peak in comparison to the aliphatic C 1s also showed close to no deviation across samples (116.9 ± 0.1 eV). This means that the chemical environment of the *N*-imidazolium is unchanged, thus it can be concluded that there was no interaction between the Pd and the nitrogen atoms of the imidazolium ring. However, after loading the polymer supports with [PdCl$_4$]$^{2-}$, an additional component became apparent between 396.4–395.9 eV, which is consistent with a Pd–N interaction, as previously reported in the deconvolution of N 1s spectra (Fig. 4b).[26–28] Quantitative analysis of the N 1s components was used to determine the amount of amine coordinated to surface Pd species in the various precatalysts which decreased in the order 84 at% (NH$_2$) > 71 at% (NH$_2$CH$_2$) > 61 at% (NMe$_2$).

Analysis of the Pd 3d core level for **2b.66** revealed a doublet attributed to divalent Pd coordinated to Cl with 3d$_{5/2}$ and 3d$_{3/2}$ peaks at 333.9 eV and 339.2 eV, respectively, as well as a shake-up satellite line at 341.1 eV.[29] An additional doublet was apparent at a higher BE with 3d$_{5/2}$ and 3d$_{3/2}$ peaks at 335.4 eV and 340.7 eV; this doublet most likely arises from Pd coordinated to aniline as the same doublet was observed for **2b**, **2b.33** and **2e**. As for the N 1s spectra, the Pd BEs were compared for the various amine supported catalysts. A shift to higher BEs was observed when the amine modified pre-catalysts **2b–2e** were compared to unfunctionalized **2a**; by comparing the separation between the Pd 3d and aliphatic C 1s BEs the Pd BEs for the various supported precatalysts was found to shift to higher BE in the following order: PIIL < NMe$_2$PIIL < NH$_2$PIIL < NH$_2$CH$_2$PIIL (Table S3, ESI†). A shift to higher BE after coordination to an amine indicates that the Pd atoms are electron deficient due to charge transfer from the Pd 3d orbitals to the amine. Moreover, the Pd 3d BEs appeared to increase with increasing loading of amine on the polymer as shown by a comparison of the ΔBE$_{(Pd–C)}$ for **2a**, **2b.33**, **2b**, **2b.66** and **2e** (Fig. 4c). A Pd–N interaction was also confirmed by solid-state ^{15}N NMR spectroscopy as the

spectrum for **1e** contained a signal at δ −323 ppm whereas the spectrum for precatalyst **2e** contained an additional signal at δ −373 ppm (Fig. S7, ESI†); similarly, a signal at δ −319 ppm in the ^{15}N NMR spectrum of **1b.66** shifted to δ −372 ppm in **2b.66** following impregnation with $[PdCl_4]^{2-}$ (Fig. S8, ESI†). The high field shift of these signals indicates that the amine has become more electron-rich, consistent with the XPS analysis of **2e** and **2b.66**.

While coordination of a heteroatom to a metal typically results in an increase in the electron density at the metal, there have been reports in which a metal has become more electron deficient due to strong metal–support interactions. For example, PdNPs on N-doped carbon nanotubes become more electron deficient by virtue of donating electrons to pyridinic nitrogen in agreement with the results described in this communication.[30] Thus, it may be possible to tune the surface electronic properties of NPs and thereby their reactivity through a judicious choice of heteroatom donor and its loading.

The Pd 3d core level of the nanoparticles recovered after *in situ* reduction of **2a–e**, typically contained two pairs of $3d_{5/2}$ and $3d_{3/2}$ doublets; the pair with $3d_{5/2}$ BEs of 330.9–331.8 eV correspond to Pd^0,[31] while those with $3d_{5/2}$ BEs of 333.24–333.9 eV are due to divalent Pd, indicating that reduction to Pd^0 was not complete. Unreduced Pd^{2+} could be indicative of Pd species strongly coordinated to Lewis basic sites that would limit their reducibility.[26] Analysis of the N 1s spectra of all samples post-catalysis revealed a loss of imidazolium nitrogen. For example, the relative contribution of imidazolium nitrogen atoms to the N 1s region decreased by 45 atm% for **2b.66** post-catalysis. This is perhaps not surprising as benzyl protecting groups are typically removed using Pd-catalysed hydrogenation. For **2a**, **2c** and **2d** the loss of imidazolium was even more significant, with no imidazolium detected at the surface of **2a** post-catalysis, this was accompanied by leaching of Pd into solution which was confirmed by ICP-OES. As such, we are currently designing more robust systems to identify catalysts suitable for use in scale-up.

In conclusion, PdNPs stabilized by aniline modified polymer immobilised ionic liquid is a markedly more efficient catalyst for the hydrogenation of CO_2 to formate than PdNPs stabilised by the individual components *i.e.* polymer immobilise ionic liquid or poly-4-aminostyrene. TOFs increased with increasing aniline content on the polyionic liquid and the optimum TOF of 500 h^{-1} is among the highest to be reported for a PdNP-based catalyst. The amine-modified PIIL motif is an encouraging design concept to develop new catalysts for the reversible hydrogenation of CO_2 and *in operando* surface investigations and detailed kinetic studies are currently underway to develop a detailed understanding of the factors that influence catalyst performance.

Conflicts of interest

There are no conflicts to declare.

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