

Ionic Liquid-Supported Pt Nanoparticles as Catalysts for Enantioselective Hydrogenation

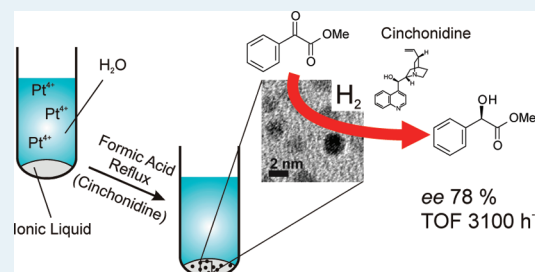
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Supporting Information

ABSTRACT: Ionic liquid (IL)-supported metal nanoparticles (NPs) are under scrutiny as novel heterogeneous hydrogenation catalysts. Here we present a simple strategy to extend the scope of these catalysts from chemoselective hydrogenation reactions to enantioselective hydrogenations. Pt nanoparticles with a mean size of 2–3 nm and narrow size distribution were obtained by stabilization with water-insoluble ILs or both an IL and cinchonidine (CD) as chiral costabilizer. High reaction rates and enantioselectivities were achieved in the hydrogenation of methyl benzoylformate (MBF). This simple synthesis protocol opens the door to catalysts based on IL-supported chiral Pt group metal NPs.

KEYWORDS: Pt nanoparticles, enantioselective hydrogenation, methyl benzoylformate, ionic liquids, cinchonidine



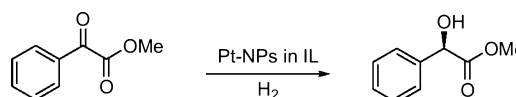
Transition metal nanoparticles (NPs) can effectively be synthesized in ionic liquids (ILs).¹ This new catalyst class has received increasing attention in the past years.^{2–5} The IL can act as a support and stabilizer against agglomeration⁶ and hence the nature of the IL has an important influence on the NP properties.^{7–9} Numerous synthesis strategies for the preparation of catalytic NPs in ILs were established; an extensive overview is provided in ref 6. When used as catalysts, purely IL stabilized NPs may tend to agglomerate as demonstrated, for example, for Pd¹⁰ or Rh¹¹ stabilized in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF₆]). The catalyst lifetime can be improved by an additional stabilizer such as polyvinylpyrrolidone,¹² solid supports,^{13,14} or by using functionalized ILs with specific stabilizing groups.¹⁵

IL-supported noble metal NPs were tested as catalysts mainly in the hydrogenation of simple substrates such as olefins or arenes.^{6,16,17} Fewer studies are available focusing on more demanding reactions such as chemoselective hydrogenations,^{18–20} and data on regioselective hydrogenations are rare.^{11,21} Investigations on enantioselective hydrogenations with IL-supported NPs as catalysts are still missing although the topic is of major interest within the field of heterogeneous catalytic hydrogenations. Pt in combination with cinchona alkaloids plays a prominent role in the enantioselective hydrogenation of activated C=O bonds²² achieving enantiomeric excesses (*ee*'s) well above 90% for selected substrates. Despite the general importance of Pt in hydrogenation catalysis, only few examples for the synthesis of simple IL stabilized Pt NPs systems forsaking the use of additional stabilizers are available.^{9,23,24}

Here, we present a straightforward protocol for the synthesis of Pt NPs stabilized by ILs. With cinchonidine (CD) as a costabilizer smaller NPs can be synthesized and chiral recognition giving rise to enantiodiscrimination is introduced,

as evidenced by the enantioselective hydrogenation of methyl benzoylformate (MBF, Scheme 1).

Scheme 1. Enantioselective Hydrogenation of MBF to (R)-Methyl Mandelate



RESULTS AND DISCUSSION

The preparation of IL stabilized NPs by reduction of H₂Pt(OH)₆ with formic acid resulted in the formation of black homogeneous suspensions using [BMIm][PF₆] and [BMIm] tris(pentafluoroethyl)trifluorophosphate ([FEP]) indicating the formation of NPs. The NPs are denoted as Pt@IL. Both ILs were not fully miscible with water and quickly picked up reduced Pt NPs from the aqueous phase. Employing water-soluble [BMIm] tetrafluoroborate ([BF₄]), only a black Pt precipitate was obtained.

To achieve enantioselectivity over heterogeneous Pt catalysts in general, the addition of a chiral modifier such as CD during the reaction is necessary. CD adsorbs strongly on Pt and hence it can also be used as a potent stabilizer for the synthesis of NPs.^{25,26} These CD-stabilized NPs were shown to act as efficient catalytic systems for the hydrogenation of ethyl pyruvate with enantioselectivities of around 80%.^{25–27} Thus, a second set of IL-supported NPs (denoted as Pt_{CD}@IL) was synthesized where CD was added as a costabilizer not only

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during the reaction but already at the stage of the NP synthesis. The synthesis worked well both with ILs insoluble and soluble in water thus also providing access to NPs supported in [BMIm][BF₄] and 1-butyl-4-methylpyridinium ([BMPy])[BF₄]. Both synthesis protocols allow the preparation of Pt NPs within 20 min (plus the time necessary for removing volatiles). There is no need for any predrying procedure of the ILs as is often described in the literature for other protocols. The solubility of the precursor in the ILs is not relevant thus making this procedure convenient and broadly applicable. Note that prior deactivation of glassware by trimethylsilyl chloride (TMSCl) was necessary to achieve good catalytic performance (vide infra).

Figure 1 shows TEM images of Pt@[BMIm][PF₆] and Pt_{CD}@[BMIm][PF₆]. NPs stabilized by only the IL featured a

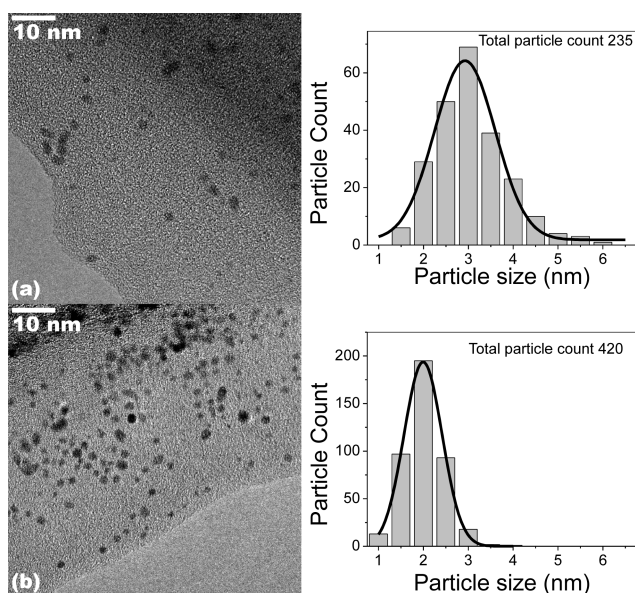


Figure 1. TEM images and size distributions of Pt@[BMIm][PF₆] (a) and Pt_{CD}@[BMIm][PF₆] (b).

Table 1. Mean Particle Sizes and FWHMs of IL-Supported Pt NPs Obtained from TEM Analysis

entry	catalyst	mean particle size (nm)	fwhm (nm)
1	Pt@[BMIm][PF ₆]	2.9	1.6
2	Pt@[BMIm][FEP]	3.1	1.6
3	Pt _{CD} @[BMIm][PF ₆]	1.8	1.1
4	Pt _{CD} @[BMIm][FEP]	1.9	1.1
5	Pt _{CD} @[BMIm][BF ₄]	2.3	1.2
6	Pt _{CD} @[BMPy][BF ₄]	2.2	1.2

mean particle size of about 3 nm (Table 1, entry 1). Particles obtained with [BMIm][FEP] were similar in size (entry 2). TEM images suggested that some primary NPs agglomerated to form chain-like structures. Using CD as a costabilizer, smaller NPs were obtained exhibiting a mean particle size of roughly 2 nm and a narrow particle size distribution (fwhm 1 nm). The similar size of NPs in all employed ILs (Table 1, entries 3–6) indicates CD to be an efficient costabilizer though the NPs derived from water-soluble ILs were slightly larger.

The catalytic performance of the IL-supported NPs was tested in the hydrogenation of MBF. Compared to the often employed pyruvate esters, MBF is less prone to undesired side reactions^{28,29} while for both substrates comparable *ee*'s were obtained over Pt/Al₂O₃.^{22,30–32} First experiments suffered from poor reproducibility. Considerably better reproducibility even from batch to batch was obtained by deactivating the glassware with TMSCl (see Supporting Information, Table S1). Strikingly, also the *ee*'s were around 10–20% higher while the TOFs increased by an order of magnitude. Similar observations were already made for Ir NPs.⁷

For NPs prepared without CD, Pt@[BMIm][PF₆] exhibited good enantioselectivity with TOFs around 800 h⁻¹, using no additional solvent and not further optimized reaction conditions (Table 2, entry 1). Note that TOFs were calculated

Table 2. Catalytic Performance of Pt NPs Supported in IL in the Enantioselective Hydrogenation of MBF^a

entry	catalyst	time (h)	conv. (%)	<i>ee</i> ^b (%)	TOF (h ⁻¹) ^c
1	Pt@[BMIm][PF ₆]	2	75	73	750
2	Pt@[BMIm][FEP]	2	81	78	810
3	Pt _{CD} @[BMIm][PF ₆]	0.5	42	76	1700
4	Pt _{CD} @[BMIm][BF ₄]	0.5	60	77	2400
5	Pt _{CD} @[BMPy][BF ₄]	0.5	70	78	2800
6	Pt _{CD} @[BMIm][FEP]	0.5	78	78	3100
7	Pt _{CD} @[BMIm][BF ₄] ^d	1	19	45	380
8	Pt _{CD} @[BMIm][BF ₄] ^e	1	45	65	900
9	Pt _{CD} @[BMIm][BF ₄] ^f	1	2.2	31	44

^aConditions: Pt/CD/MBF 1/5/2000 (molar ratios), 25 °C, 30 bar H₂. ^b(*R*)-selective. ^cTOFs were calculated based on the overall Pt amount. ^dNo extra CD added. ^eHAc added (MBF/HAc 1/4.4 (mol/mol)). ^fAddition of 5 wt. % [BMIm]Cl to [BMIm][BF₄].

based on the overall amount of Pt, thus serving as a measure of the efficacy with which the noble metal was used. Slightly higher *ee*'s and similar TOFs were measured with Pt@[BMIm][FEP] (entry 2). When CD was employed already at the stage of the NP synthesis, significantly higher TOFs were obtained from the smaller NPs (entries 3–6). Regardless of the IL, the *ee*'s were similar and additionally close to those with Pt@[BMIm][FEP] suggesting that the type of IL does not affect the enantioselection significantly. Note that in all cases the addition of CD was necessary to avoid particle agglomeration and poor catalytic performance (entry 7). Though the type of IL had only little influence on the particle size, the catalytic activity was clearly affected and followed the order [BMIm][PF₆] < [BMIm][BF₄] < [BMPy][BF₄] < [BMIm][FEP] reaching a high TOF of 3100 h⁻¹. This high TOF is especially noteworthy since in control experiments with Pt/Al₂O₃ the MBF hydrogenation rate dropped from 210 h⁻¹ (in toluene) to only 3 h⁻¹ (in [BMIm][BF₄]) at 10 bar.

Because of the complexity of IL-supported NP systems, an interpretation of the superior performance of Pt@[BMIm][FEP] is not straightforward. One possible explanation might be the higher stability of the [FEP] anion against hydrolysis³³ compared to the [BF₄] and [PF₆] anions generating HF³⁴ but also a weaker interaction with the Pt-cinchona system might be conceivable. Surprisingly, acetic acid, which is known to be a good solvent for this reaction, decreased the catalytic performance (entry 8). This might be explained by the already present formic acid from the NP synthesis known to promote

the reaction when used as an additive.³⁵ Acetic acid as an additional weak acid thus does not give rise to any further beneficial effects. Since hydrogenation reactions over Pt group metals may be sensitive to the presence of halides,¹⁹ we tested the effect of small amounts of [BMIm]Cl on the reaction, which strongly poisoned the catalyst (entry 9).

Pt_{CD}@[BMIm][FEP] was tested for reusability (Figure 2). The performance of the NPs was stable between the first two

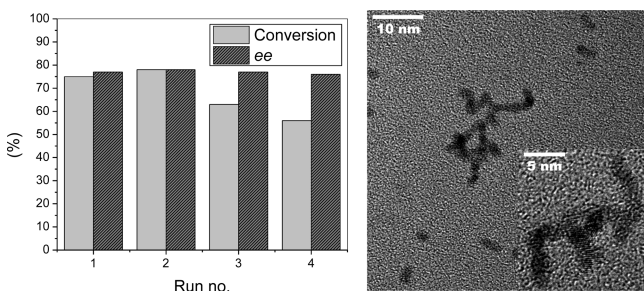


Figure 2. Conversion and *ee* in four consecutive runs using Pt_{CD}@[BMIm][FEP] (left) and TEM image recorded after the fourth run (right). Conditions: Pt/CD/MBF 1/5/2000, 25 °C, 30 bar H₂, 0.5 h reaction time.

runs. The conversion declined slightly in the third run while the *ee* remained stable. After 4 runs, a total turnover number of 5400 was obtained. The TEM investigations revealed that some NPs agglomerated to form worm-like structures resulting in a lower active surface area (Figure 2).

The group of Bönemann was the first to recognize the potential of CD as a stabilizer for Pt NPs. We thus compared our best catalyst (Table 3, entry 1) with Pt NPs prepared from

Table 3. Comparison of NPs in IL with Other Heterogeneous Pt Catalysts^a

entry	catalyst	time (h)	conv. (%)	<i>ee</i> ^b (%)	TOF (h ⁻¹) ^c
1	Pt _{CD} @[BMIm][FEP]	0.5	78	78	3100
2	Pt-NPs ^d	1	45	59	900
3	Pt _{CD} -NPs ^e	0.5	54	76	2200
4	5%Pt/Al ₂ O ₃ ^f	0.5	40	87	1600
5	5%Pt/Al ₂ O ₃ ^g	0.5	11	61	460

^aConditions: Pt/CD/MBF 1/5/2000 (molar ratios), 25 °C, 30 bar H₂. ^b(*R*)-selective. ^cTOFs were calculated based on the overall Pt amount. ^dPt-NPs synthesized according to ref 25. ^eUnsupported NPs from H₂Pt(OH)₆ with CD. ^fPretreated in flowing H₂ at 400 °C as described in ref 40. ^gUsed without pretreatment.

PtCl₄²⁵ as described by Bönemann (entry 2) and similar CD-stabilized NPs not supported in an IL obtained from H₂Pt(OH)₆ according to our protocol (entry 3). The NPs obtained from PtCl₄ gave lower *ee* and rate which might be connected to the strong adsorption and poisoning effect of chloride (vide supra). NPs from H₂Pt(OH)₆ resulted in the same *ee* as Pt_{CD}@[BMIm][FEP] but a lower TOF which might be related to the stabilizing effect of the IL. The commonly used commercial Pt/Al₂O₃ catalyst afforded an *ee* of around 10% higher (entry 4) but only after high temperature treatment in H₂ increasing the *ee* by 26% compared to the untreated catalyst (entry 5). For obvious reasons high temperature treatment is not possible for Pt@IL. The overall high activity of the IL-supported NPs suggests that the IL acts as an optimal

stabilizer allowing the efficient synthesis of NPs but not compromising the catalytic performance. The enantioselectivity is among the highest achieved over quasihomogeneous Pt NPs: other Pt NPs-stabilizer systems^{25,36–39} tested in the enantioselective hydrogenation of ethyl pyruvate as a similar substrate resulted in *ee*'s between 50 and 78%.

CONCLUSIONS

We have successfully synthesized various IL stabilized Pt NPs. The NP size can be tuned by employing a chiral costabilizer opening the possibility of chiral recognition. This approach results in an effective catalyst for the hydrogenation of activated ketones. The use of deactivated glassware was required for obtaining reliable data. MBF was hydrogenated with *ee*'s close to 80% and TOFs of up to 3100 h⁻¹. Without any preactivation or addition of an organic solvent, the catalyst provided higher rate and *ee* in the hydrogenation of MBF than the widely used, commercially available Pt/Al₂O₃ reference catalyst. The potential of this catalytic system for other hydrogenation reactions is currently being investigated.

EXPERIMENTAL SECTION

Pt NPs in IL were synthesized under N₂ atmosphere from H₂Pt(OH)₆ by reduction with formic acid in a refluxing mixture of water and either [BMIm][PF₆] or [BMIm][FEP]. When the precursor was fully reduced after 10 min, volatiles were removed to obtain a dark black suspension. The NPs are denoted as Pt@IL. NPs synthesized with additional CD as costabilizer are denoted as Pt_{CD}@IL, utilizing [BMIm][PF₆], [BMIm][FEP], [BMIm][BF₄], and [BMPy][BF₄] as supports. The catalytic hydrogenation of MBF was conducted at room temperature and 30 bar H₂ in a mixture of NPs in IL, CD, and MBF usually in the absence of additional solvents. Details are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental section, influence of glass deactivation on catalytic performance. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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