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Tuning the Chemoselective Hydrogenation of Nitrostyrenes Catalyzed by Ionic Liquid-Supported Platinum Nanoparticles

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Ⓢ *Supporting Information*

ABSTRACT: Pt nanoparticles (NPs) in the range of 1.7−3.4 nm were synthesized in an ionic liquid (IL). Subsequent immobilization on various solid supports (silica, alumina, titania, carbon nanotubes (CNTs)) in some cases proved to be beneficial. These catalysts exhibited excellent performance in the chemoselective hydrogenation of 3-nitrostyrene. The presence of the IL, the reaction medium (acidic or basic), and the type of support greatly influenced the catalytic behavior. Yields exceeding 90% to either 3-ethylnitrobenzene under acidic conditions or 3-aminostyrene under basic conditions could be achieved. The reaction proceeded smoothly at room temperature and 1 bar of hydrogen pressure with turnover frequencies in the range of 100 h^{-1}. The NP catalysts could be reused efficiently by supporting them either on SiO$_2$ or on CNTs. Comparison with IL-free catalysts indicated the principal influence of the IL on the selectivity.

KEYWORDS: platinum catalysis, chemoselective hydrogenation, ionic liquids, nitrostyrene, nitrobenzene, acid−base switch, carbon nanotubes, aniline derivatives
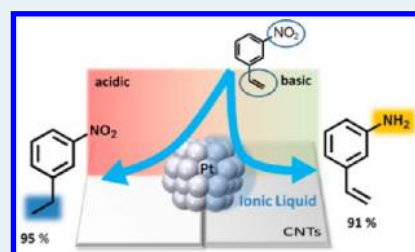
INTRODUCTION

After the discovery that ionic liquids (ILs) can stabilize metal nanoparticles (NPs),[1] numerous investigations targeted at the use of these novel IL-stabilized NPs as catalysts.[2−6] In most studies simple test reactions, such as the hydrogenation of cyclohexene,[1,7,8] were applied to probe the catalytic behavior. An inherent disadvantage of ILs is the often low solubility of hydrogen,[9,10] which can lead to lower hydrogenation rates. This can be overcome to some extent by supporting ILs on solid materials.[11] The true chance of this novel class of catalysts lies in improved selectivities as has been demonstrated, e.g., for selective hydrogenation reactions.[12−15] The chemoselective hydrogenation of molecules containing several reducible groups is an important challenge in heterogeneous catalysis, and among other parameters, it is often influenced by the type of solid support.[16−18] Ionic liquids as a novel tunable catalyst component which can act as a support and/or stabilizer might therefore give rise to improved catalysts.

An industrially important reaction where the support influence[16,19] has been heavily discussed is the hydrogenation of a nitro group in the presence of other reactive groups. Besides the proper choice of support, a key to success has been the design of optimized catalysts, e.g., by the addition of suitable modifiers[20,21] and/or applying carefully adjusted pretreatment conditions.[22] This way, amino compounds with a wide variety of reducible functional moieties, including carbonyl, halide, and nitrile functionalities, are accessible.[21,23] Compounds bearing both a C=C double bond and a nitro group have proven to be a particularly demanding challenge.[21,24] Both functional groups are readily hydrogenated, and thus, achieving high selectivity for either group at high conversion is difficult. Several attempts to tackle this challenge rely on either decreasing the catalyst activity significantly or using metals with low catalytic activity. Siegrist et al.[25] achieved high selectivity for the nitro group with heterogeneous Pt catalysts modified either by H$_3$PO$_2$ and V or by Pb and FeCl$_2$. Rather harsh reaction conditions were necessary, indicating that the additives partially deactivated the catalyst. Gold[26−28] and silver[29] catalysts possessing in general lower hydrogenation activity than Pt also afford high selectivity for the nitro group without the need for additives but require more forcing reaction conditions. Corma et al.[22] demonstrated that high selectivity for the nitro group can also be achieved on Pt catalysts by decorating, i.e., selectively deactivating,[30] the Pt surface with the support material. Poisoning a Pt catalyst with sulfur-containing additives also enables the selective hydrogenation of the nitro group.[31,32] In most of these studies, the metal particle size and especially the choice of support were crucial, and a strong metal−support interaction was deemed necessary for high selectivity of the reduction of the nitro group to the corresponding amino group. Arguably, due to the less significant industrial importance, the chemoselective hydro-

genation of a C=C double bond in the presence of a nitro group has been focused on to a much lesser extent. Only a few examples report on Rh,[33] Pd,[34] or Au[35] complexes achieving high selectivities at close to full conversion.

Where the interaction between the support and active metal is important, IL-supported NPs might offer interesting new opportunities for tuning selectivities in demanding reactions. Here we tested the potential of IL-stabilized Pt NPs as selective catalysts for the hydrogenation of 3-nitrostyrene. While in previous studies high selectivity was obtained by focusing on the optimization of the catalyst, we demonstrate that full reversion of the selectivity for either C=C or nitro group hydrogenation can be obtained by proper choice of the reaction conditions.

■ EXPERIMENTAL SECTION

Chemicals and Materials. All chemicals were used as received. Tetrahydrofuran (THF; ≥99.5%), diethyl ketone (DEK; ≥99%), dichloromethane (DCM; ≥98%), ethyl acetate (EtOAc; ≥99.5%), N,N-dimethylformamide (DMF; ≥99.8%), CHCl₃ (≥99.8%), 2,2′-bipyridine (≥99%), and triethylamine (99.5%) were purchased from Sigma-Aldrich. Quinoline (≥99%) was obtained from Aldrich. 1,2-Dichlorobenzene (DCB; 99%), cyclohexane (extra pure), 3-nitrostyrene (NS; 97%), and dodecane (99%) were purchased from Acros. Chlorotrimethylsilane ((TMS)Cl; 98+%) was obtained from Alfa Aesar. H₂Pt(OH)₆ (99.9%) was provided by both Alfa Aesar and Johnson Matthey. Acetic acid (≥99.5%), trifluoro-acetic acid (TFA; >98%), toluene (≥99.7%), and 5% Pt/C (catalog no. 80982-14, prereduced in H₂ at 200 °C) were provided by Fluka. Ethanol (absolute) was from Alcosuisse. Merck provided 1,10-phenanthroline (anhydrous), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([BMIm][FEP]; high purity) and formic acid (98−100%). Strem Chemicals provided 5% Pt/SiO₂ (ESCAT 2351, prereduced in H₂ at 200 °C). Engelhard supplied 5% Pt/Al₂O₃ (no. 4759, prereduced in H₂ at 400 °C) and Al₂O₃ (no. 43299; pellets were crushed prior to use). Multiwalled carbon nanotubes (CNTs; diameter 20−40 nm, length 5−15 μm) were purchased from TCI Deutschland. SiO₂ (Aerosil 300) and TiO₂ (P 25) were from Evonik. All glassware involved in the handling of NPs in IL was deactivated with (TMS)Cl as described previously.[36]

Synthesis of Pt NPs Stabilized by IL. Pt NPs were formed by reduction of H₂Pt(OH)₆ with formic acid. In detail, Pt NPs were synthesized by adding 46 mg of the Pt precursor (H₂Pt(OH)₆) in 40 mL of refluxing water in a previously deactivated Schlenk tube[36] to form a dispersion. After 20 min 1.0 mL of [BMIM][FEP] was added. A solution of 40 mg of quinoline (resulting in a costabilizer:Pt molar ratio of 2:1) in 10 mL of 0.5 M formic acid was added with vigorous stirring at 1000 rpm. The mixture turned black after a few minutes, indicating reduction of the Pt precursor. After 15 min of reflux, the mixture was cooled to room temperature (rt), and volatiles were slowly removed overnight. Finally, the Pt NPs in IL were dried under high vacuum for 2 h. Depending on the costabilizer used, the catalysts are denoted as Pt@IL (no costabilizer), Pt-Q@IL (quinoline), Pt-B@IL (2,2′-bipyridine), and Pt-P@IL (1,10-phenanthroline). The nominal Pt loading was 2% (w/w) on the basis of the mass of the IL. Note that H₂Pt(OH)₆ obtained from Alfa Aesar could not be dispersed and required slightly different handling; thus, dissolution of the Pt precursor in dilute NaOH as described in our previous report[36] was

necessary. Note that due to the later addition of formic acid also in this case a dispersion (not a solution) of H₂Pt(OH)₆ was formed directly prior to reduction.

Deposition of Pt NPs on Solid Supports and Reuse Experiments. The deposition of the Pt NPs was done directly before the reaction was started. Thus, the solid support was added to the premixed reaction mixture (consisting of substrate, solvent, standard, and Pt-X@IL) under vigorous stirring. The nominal loading of the IL was 30 mg/100 mg of solid support. This refers to a mass fraction of 23%. The catalysts are denoted as Pt-X@IL/support ("X" specifying the type of stabilizer; see the section "Synthesis of Pt NPs Stabilized by IL").

Preparation of Pt/CNTs. A 138 mg portion of CNTs was dispersed in 2.5 mL of water and refluxed for 15 min. A 2.1 mg sample of H₂Pt(OH)₆ was added and the dispersion refluxed for another 15 min. Afterward 0.62 mL of a 0.5 M formic acid solution containing 23 μmol/mL quinoline (corresponding to a quinoline:Pt ratio of 2:1) was added. The mixture was refluxed for 1 h. Volatiles were removed slowly overnight, and the catalyst was finally dried in high vacuum over several hours.

Hydrogenation of 3-Nitrostyrene. In a typical run ca. 30 mg of Pt@IL was added to a previously deactivated[36] glass flask. A ca. 30 mg sample of n-dodecane was added together with the appropriate amount of NS to achieve the desired substrate-to-catalyst molar ratio (typically NS:Pt = 250:1). Solvent was added accordingly to obtain a substrate concentration of 0.47 mol/L. If a solid support was used, it was added at this stage under vigorous stirring to obtain a nominal IL loading of 30 mg/100 mg of solid support. The mixture was stirred under a N₂ atmosphere. After 15 min, stirring was stopped, and the flask was slowly flushed with H₂ for 5 min. The reaction was started by beginning the stirring at 750 rpm. Samples for GC analysis were taken in regular intervals. GC analysis was performed with an HP 6000 series gas chromatograph equipped with a flame ionization detector (FID) and an HP-5 GC column (Agilent Technologies Inc.). Selectivities for 3-ethylnitrobenzene (ENB), 3-aminostyrene (AS), and 3-ethylaniline (EA) were determined using n-dodecane as the internal standard using commercially available authentic samples. The mass balance was closed (>95%), showing that GC analysis was suitable as an analysis technique. For better comprehensiveness, the intermediate selectivity is sometimes provided, which is calculated as the difference of the combined selectivities of ENB, AS, and EA from 100%. The turnover frequency (TOF) was calculated on the basis of the total Pt amount and thus represents a conservative estimate. With CNTs a blind test was performed showing no catalytic activity.

Reuse Experiments. Reuse experiments were conducted with catalysts supported on solid supports. For catalyst reuse, the reaction mixture was treated under mild vacuum to remove the solvent. A ca. 10 mL volume of toluene/cyclohexane (1:1) was added to the catalyst, and the suspension was filtered. The catalyst was washed with toluene/cyclohexane until no further substrate or product could be found in the filtrate (using GC analysis). The catalyst was then dried overnight under a reduced atmosphere.

Transmission Electron Microscopy (TEM). The NPs supported in IL were diluted in acetophenone and deposited on a holey carbon film supported on a copper grid. Solid catalysts were dispersed in ethanol. Measurements were performed on a Tecnai F30 microscope (FEI, field emission gun operated at

300 kV). The particle size distribution was automatically calculated using the ImageJ 1.40 g software package (National Institutes of Health, Bethesda, MD) after manual enhancement of the contrast. The mean particle size was obtained from Gaussian fitting, where the full width at half-maximum (fwhm) is provided as a measure of the broadness of the particle size distribution.

RESULTS

Hydrogenation of 3-Nitrostyrene with Pt NPs Stabilized by IL. Our previous studies showed that the hydrophobic IL [BMIm][FEP] is a beneficial stabilizer featuring good chemical stability[37] while not interfering strongly with the catalytic performance of the active phase.[38] With this IL, Pt NPs can be obtained by formic acid reduction of $H_2Pt(OH)_6$ in water (denoted as Pt@IL). TEM analysis indicated an average particle size of 3.4 nm (fwhm = 1.2 nm), which is in good agreement with that from our previous study.

A preliminary set of experiments showed that Pt@IL hydrogenated the ethylene moiety of styrene around 4 times faster than the nitro group of nitrobenzene in a competitive hydrogenation, while a widely used commercial 5% Pt/Al$_2$O$_3$ catalyst used for reference exhibited negligible hydrogenation preference (see the Supporting Information). In the next step, we employed NS as a test substrate combining both the C=C and the NO$_2$ moieties in a single molecule. The reactions were carried out at rt and 1 bar of hydrogen pressure. The reaction scheme is rather complex due to the two major reaction pathways and since hydrogenation of the nitro group can proceed stepwise. A simplified version showing only the main intermediates observed in this study, i.e., the N-hydroxylamines, is given in Scheme 1. A more detailed scheme on NO$_2$ group hydrogenation can be found elsewhere.[39] Under the reaction conditions used, the IL-supported Pt NP catalyst retained its

Scheme 1. Simplified Hydrogenation Pathways of NS Based on Identified Products in the Reaction Mixture[a]
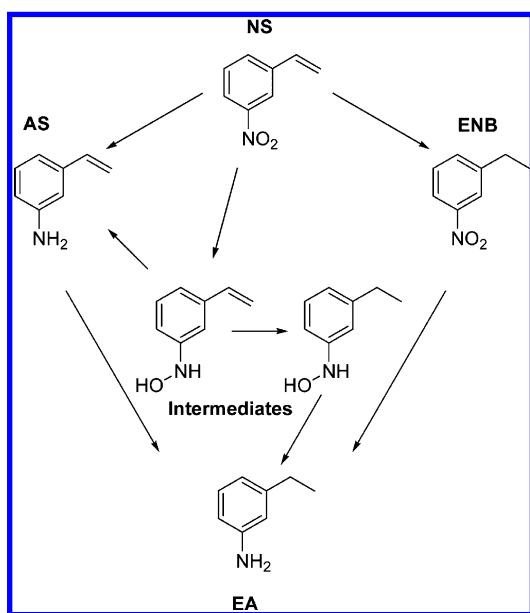
[a]Either the C=C bond or the NO$_2$ group can be hydrogenated, the latter reaction giving rise to either the amine (AS and EA) or intermediate hydrogenation products, i.e., mainly the hydroxylamines. Note that arrows in this scheme do not imply single steps.

preferential activity for the C=C double bond. The selectivity for ENB of this catalyst was only moderate and continuously decreased with conversion (Figure 1), reaching a value of 61%
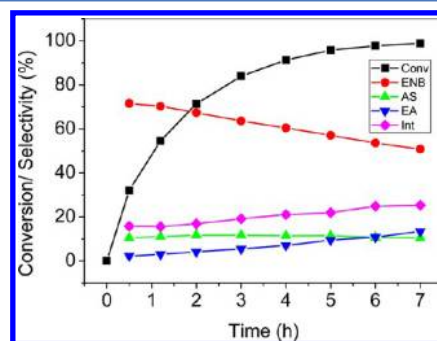
Figure 1. Conversion and selectivity in the hydrogenation of NS with Pt@IL. Conditions: NS:Pt = 250:1 (mol/mol), rt, 1 bar of H$_2$ in THF (NS concentration 0.47 mmol/mL). Conv = conversion of 3-nitrostyrene, ENB = 3-ethylnitrobenzene, AS = 3-aminostyrene, EA = 3-ethylaniline, and Int = intermediates (mainly N-hydroxylamines).

at around 90% conversion. Under the same reaction conditions, the 5% Pt/Al$_2$O$_3$ reference catalyst exhibited no preferential selectivity for any of the possible hydrogenation products at high conversion (see the Supporting Information).

Influence of Additional Stabilizers. During the hydrogenation reaction, the Pt NPs evidently agglomerated, which may at least be partly responsible for the continuous decrease in selectivity for ENB during the reaction. In our previous study,[36] the catalytic performance and especially the stability of the Pt NPs against agglomeration could be improved by using cinchonidine (CD) as a costabilizer. The chiral quinuclidine moiety of CD is not required in this study, and thus, we applied only its strongly adsorbing aromatic unit,[40] quinoline, as an additional stabilizer during the NP synthesis. The catalyst is denoted as Pt-Q@IL. Two similar polyaromatic heterocycles, i.e., 1,10-phenanthroline (Pt-P@IL) and 2,2′-bypyridine (Pt-B@IL), were additionally tested as costabilizers. The bidental ligands required longer reduction times for the NP synthesis and prevented the formation of NPs when PtCl$_4$ was used as a catalyst precursor. Note that the NPs were synthesized under acidic conditions, so the stabilizers were present in protonated form after synthesis.

By the addition of the costabilizers, the size of the Pt NPs could be decreased (Figure 2). With both 1,10-phenanthroline and quinoline, NPs with an average size slightly below 2 nm were obtained; 2,2′-bipyridine afforded larger NPs with an average size of 2.4 nm (see the Supporting Information).

The application of an additional stabilizer indeed improved the catalytic performance (Table 1, entry 1 vs entries 2−4). Pt-B@IL afforded the highest selectivity for ENB. Pt-Q@IL gave the highest reaction rate and a slightly higher selectivity for NO$_2$ group hydrogenation. The performance of Pt-P@IL was significantly poorer with respect to both reaction rate and selectivity.

Variation of the Solvent. While the substrate-to-catalyst ratio had only little influence on the selectivity for ENB and the overall reaction rate (see the Supporting Information), the choice of solvent affected the catalytic behavior in a more pronounced way, though mostly maintaining the preferential selectivity for ENB (Table 2; for a full list see the Supporting Information). Toluene facilitated a higher ENB selectivity, but
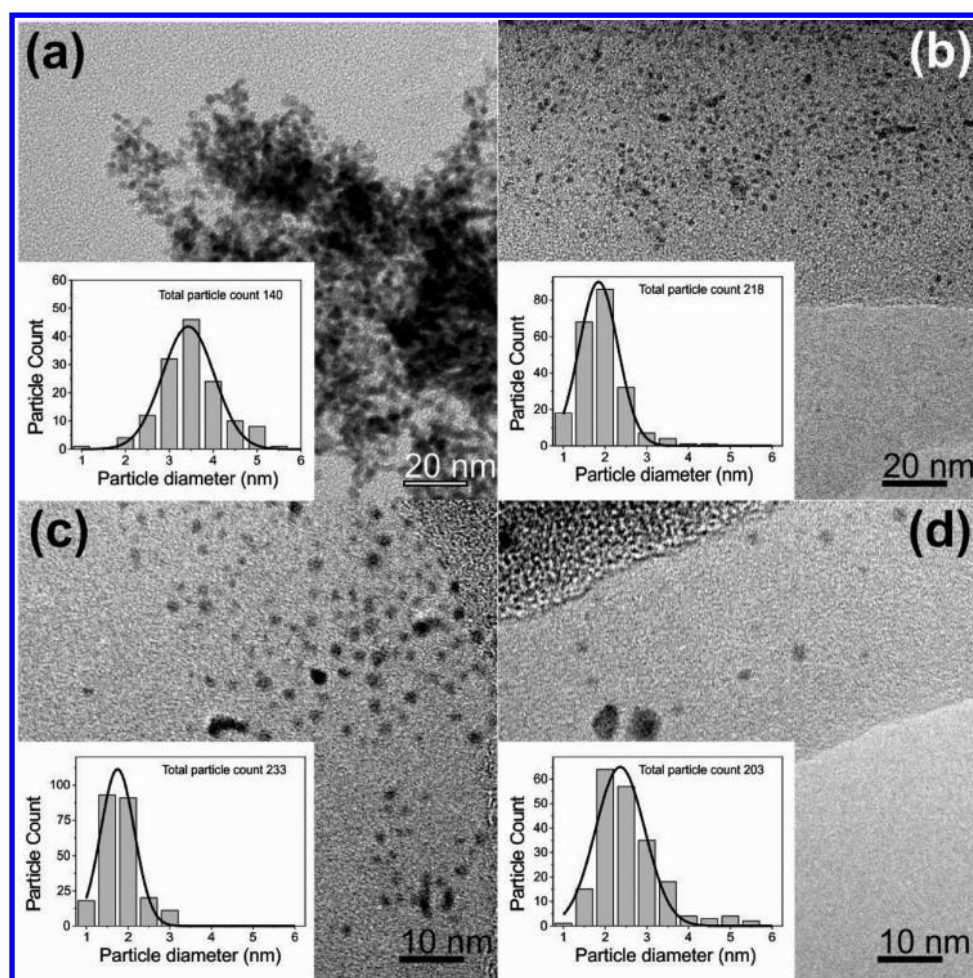
Figure 2. TEM images and particle size distributions (insets) of Pt@IL (a), Pt-Q@IL (b), Pt-P@IL (c), and Pt-B@IL (d) stabilized by IL (a) and additionally quinoline (b), 1,10-phenanthroline (c), and 2,2′-bipyridine (d).

Table 1. Effect of the Stabilizer on the Hydrogenation of NS[a]

entry	catalyst	conv (%)	ENB selectivity (%)	AS selectivity (%)	EA selectivity (%)	TOF (h^{-1})	reaction time (h)
1	Pt@IL	91	61	11	6	56	4
2	Pt-B@IL	90	83	3.1	3.4	110	2
3	Pt-Q@IL	88	81	3.4	5	260	0.8
4	Pt-P@IL	79	74	2.2	6.5	80	2.5

[a]Conditions: NS:stabilizer:Pt = 250:2:1 (mol/mol), rt, 1 bar of H$_2$ in THF (NS concentration 0.47 mmol/mL).

Table 2. Effect of the Solvent on the Hydrogenation of NS[a]

entry	solvent	conv (%)	ENB selectivity (%)	AS selectivity (%)	EA selectivity (%)	TOF (h^{-1})
1	toluene	90	90	0.4	10	24
2	THF	90	83	3.1	3.4	110
3	EtOAc	92	92	1.4	3.1	120
4	CHCl$_3$	88	98		2.4	20
5	DCB	92	94		5.2	25
6	DCB[b]	90	67	4.4	23	38
7	EtOAc[c]	100	95		3.3	140

[a]Conditions: NS:Pt-B@IL = 250:1 (mol/mol), rt, 1 bar of H$_2$ in solvent (NS concentration 0.47 mmol/mL). [b]Na$_2$CO$_3$ (50 mg) added. [c]Trifluoroacetic acid (0.05 M) added.

good activity were obtained in EtOAc (entry 3). Chlorinated solvents (entry 4 and 5) gave ENB with the highest selectivity, though at low reaction rate.

The high selectivity for ENB observed with chlorinated solvents is interesting. Chlorinated solvents may undergo reductive dehalogenation[41] over Pt catalysts, thus forming traces of HCl. The addition of chloride (as [BMIm]Cl)) during the reaction or already at the stage of the NP synthesis only decreased the reaction rate without significantly affecting the selectivity. We thus decided to test the effect of the acidity in other solvents. Indeed, the addition of Na$_2$CO$_3$ to DCB as an acid scavenger decreased the selectivity for ENB greatly (entry 6). On the contrary, the addition of a strong acid (here TFA was used) to, e.g., EtOAc, increased the selectivity for ENB (cf. entries 3 and 7), circumventing the use of chlorinated solvents. This way, ENB could be obtained with 95% selectivity even at full conversion with a significantly higher TOF than in

the reaction rate was low (entry 1). In THF the reaction rate was higher (entry 2), and both good selectivity for ENB and

chlorinated solvents. Note that addition of the acid led to precipitation of the NPs in EtOAc. While the choice of solvent was crucial for the catalyst's selectivity, more forcing conditions in terms of temperature and pressure mainly increased the reaction rate. Provided that the reaction was stopped timely, the selectivity for ENB was only slightly lower compared to that from the experiment at 1 bar of H_2 and rt and remained above 90% at high conversion (see the Supporting Information).

Pt NPs on Solid Supports. Various publications[22,29,30] emphasize the influence of the support material on the hydrogenation activity and selectivity of nitroaromatics. Immobilizing the same type of NPs on different supports allows the support influence to be studied in a more consistent manner. After addition to the reaction mixture (prior to the reaction being started), the solid support led to rapid decolorization of the black reaction mixture, suggesting rapid adsorption of the NPs on the solid support materials, which is also inferred by the darkening of white supports. Adsorption of the NPs is further suggested by TEM images of the dried powders (see the Supporting Information). Using THF as a relatively inert solvent, the choice of solid support had a great influence on the catalytic performance (Figure 3). With SiO$_2$,
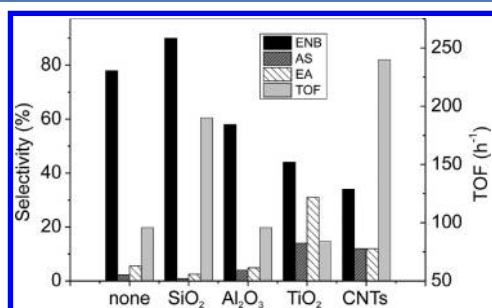

Figure 3. Effect of a solid support on the selectivity and reaction rate in the hydrogenation of NS at high conversion (95−98%). Conditions: NS:Pt: = 500:1 (mol/mol), catalyst Pt-B@IL in THF (substrate concentration 0.47 mmol/mL), 1 bar of H_2, rt, solid support added to achieve an IL loading of 30 mg/100 mg of solid support (Pt loading 0.4% (w/w)). Selectivity for intermediates is not shown.

which is (without special pretreatment[42]) a relatively inert support,[43] the reaction was selective for ENB. The selectivity was even higher than in the absence of SiO$_2$, which might be due to the stabilizing influence of the support. On the other hand, supports such as Al$_2$O$_3$, TiO$_2$, and CNTs, which are generally expected to interact stronger with the metal, gave much lower selectivities for ENB and led to considerable hydrogenation of the NO$_2$ group to the amine. Also intermediates, especially the *N*-hydroxylamines, were accumulated. Noticeably, the support material influenced the reaction rate. The enhancement of the reaction rate by addition of some solid support might result from the further stabilization of the NPs against agglomeration.[36] It might however also originate from a non-negligible adsorption of the nitroaromatic compounds on the support as shown by Corma et al.[27] With the addition of CNTs, the highest turnover frequencies of the substrate were observed.

Reversing the Selectivity by an Acid−Base Switch. The previous experiments showed that acidic conditions promote the hydrogenation of the vinyl group in NS, which led us to the assumption that basic conditions might promote the reverse selectivity. Indeed, the use of triethylamine as a solvent led to a very different reaction pathway (Figure 4).
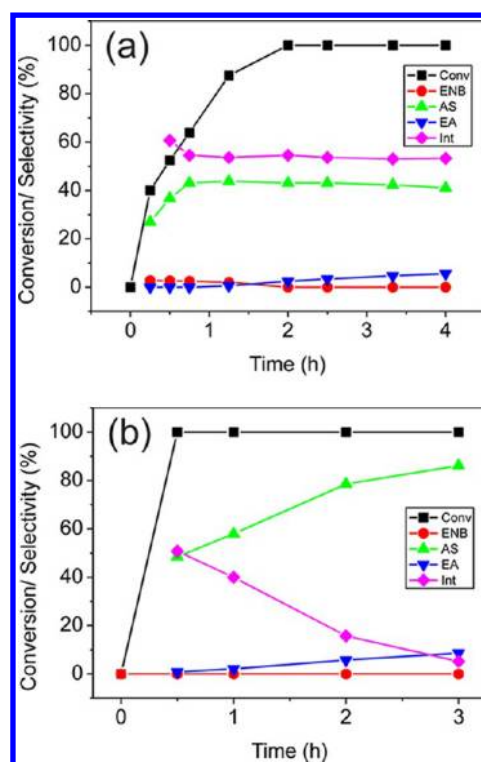
Figure 4. Reaction pathway of the hydrogenation of NS in NEt$_3$ with Pt-B@IL (a) and Pt-B@IL supported on CNTs (b). Conditions: NS:Pt = 500:1 (mol/mol), catalyst Pt-B@IL/CNTs in NEt$_3$ (substrate concentration 0.47 mmol/mL), 1 bar of H_2, rt.

While the hydrogenation rate of the vinyl group was low, mostly the nitro group was hydrogenated to give a mixture of AS and intermediates typically occurring in nitrobenzene hydrogenation, the dominating intermediate being 3-(*N*-hydroxylamino)styrene.[19] In this way, with the same Pt NP catalyst, a complete reversion of the selectivity from C═C hydrogenation to NO$_2$ hydrogenation could be achieved by adequate choice of the reaction conditions. The formed intermediates were, however, barely converted to the amine, the overall reaction rate becoming very low (the TOF for the conversion of 3-(*N*-hydroxylamino)styrene was >10 h^{-1}) once full conversion of the substrate was reached (Figure 4a). This suggests that the previously formed AS mainly resulted from hydrogenation of NS with only a small contribution by AS formed via 3-(*N*-hydroxylamino)styrene hydrogenation (which is found in the solution). Thus, while virtually only the nitro group was hydrogenated, the overall selectivity for AS remained poor, reaching 44% at maximum. At longer reaction times, the selectivity naturally decreased because overhydrogenation became an issue. By exploiting the previously observed shift to NO$_2$ hydrogenation by supporting the Pt NPs on CNTs, a much higher selectivity for AS of 86% could be obtained (Figure 4b). CNTs not only made the reaction faster but also promoted the preferential hydrogenation of the major intermediate, i.e., 3-(*N*-hydroxylamino)styrene, to the desired AS. A slightly increased yield of AS could be obtained by using NPs derived from stabilization with quinoline (Table 3). The selectivity for AS could be further improved by doubling the amount of IL, resulting in a maximum selectivity of above 90% for AS (entry 3). Again, more forcing conditions in terms of pressure and temperature affected the selectivity for AS only

Table 3. Comparison of Pt-B@IL and Pt-Q@IL Supported on CNTs in the Hydrogenation of NS with Respect to the Maximum AS Yield[a]

entry	catalyst	ENB yield (%)	AS yield (%)	EA yield (%)
1	Pt-B@IL/CNTs	0	86	8.7
2	Pt-Q@IL/CNTs	0	89	11
3	Pt-Q@IL/CNTs[b]	0	91	9.7

[a]Conditions: NS:Pt = 500:1 (mol/mol), catalyst as indicated in NEt_3 (substrate concentration 0.47 mmol/mL), 1 bar of H_2, rt. [b]Addition of extra [BMIm][FEP] (30 mg/100 mg with respect to the CNTs), thus twice the amount of IL compared to that of the previous experiment.

slightly (see the Supporting Information), resulting, however, in much higher reaction rates.

Catalyst Reuse. Catalyst reuse was checked for Pt-Q@IL under both acidic and basic conditions. For the study under acidic conditions, the NPs were supported on SiO_2. The catalyst showed good reusability (Figure 5). Additional
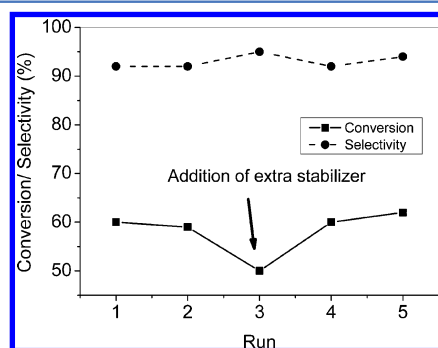
Figure 5. Reuse experiments of catalyst Pt-Q@IL supported on SiO_2 under acidic conditions: conversion and selectivity after 30 min of reaction time. Quinoline (quinoline:Pt = 2:1 (mol/mol)) was added in the third run. Conditions: NS:Pt = 500:1 (mol/mol), catalyst Pt-Q@IL/SiO_2, 0.05 M TFA in EtOAc (substrate concentration 0.47 mmol/mL), 1 bar of H_2, rt.

quinoline applied in the third run decreased the reaction rate slightly, showing that the costabilizer adsorbed on the Pt surface (which is important for the NP stabilization during the synthesis; cf. Figure 2) but did not have any significant influence on the selectivity. The catalyst approached normal activity again in the next runs when no additional quinoline was added. For the reuse study under basic conditions, Pt-Q@IL was immobilized on CNTs (Figure 6). From run to run, the
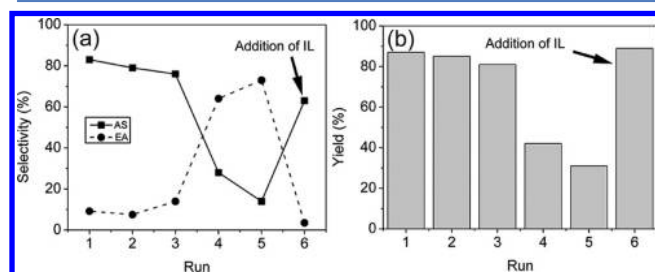
Figure 6. Reuse experiments of catalyst Pt-Q@IL supported on CNTs under basic conditions: selectivity after 3 h of reaction time (a) and maximum yield of AS (b). Conditions: NS:Pt = 500:1 (mol/mol), catalyst Pt-Q@IL/CNTs, NEt_3 (substrate concentration 0.47 mmol/mL), 1 bar of H_2, rt.

catalyst converted both the substrate and the intermediates faster. This occurs, however, at the cost of the selectivity for AS. We assumed that removal of the IL during catalyst washing (though done with an apolar solvent mixture, i.e., toluene/cyclohexane, 1:1) might be one reason for our observation. Indeed, addition of [BMIm][FEP] in the sixth run (Figure 6a) reversed the previously observed trend, resulting in a catalyst with close to initial activity with a maximum yield of AS as obtained in the first run (Figure 6b), suggesting that the catalyst system under basic conditions is principally also recyclable. This demonstrates the important role of the IL for achieving high selectivities for AS. Note that addition of extra quinoline as stabilizer had barely any influence.

Selectivity Switch over Conventional Heterogeneous Catalysts. The previous experiments demonstrated that the hydrogenation route of NS can be controlled by either basic or acidic conditions, the choice of support, and the use of an IL. We were interested in whether the observed principles could also be applied to more common heterogeneous catalysts, which additionally allows for studying the IL effect in a more isolated manner. Figure 7 shows that over commercial 5% Pt/
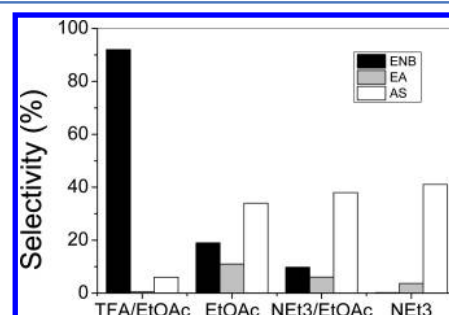

Figure 7. Selectivity switch by using acid or base over 5% Pt/SiO_2. Conditions: 10 mg of 5% Pt/SiO_2, 190 mg of NS, 2.4 mL of solvent (where applicable with 0.05 M TFA or NEt_3), rt, 1 bar of H_2, conversion >90%. Selectivity for intermediates is not shown.

SiO_2 the major reaction pathway is also affected by the presence of acid or base in EtOAc. The same trend but with lower selectivities was observed with THF as a solvent (see the Supporting Information). The addition of an IL under acidic conditions had barely any influence on the selectivity (Supporting Information) in the hydrogenation to ENB, showing that the IL is mainly important under basic conditions.

The courses of the reaction over four different catalysts, i.e., 5% Pt/C, 5% Pt/Al_2O_3, 5% Pt/SiO_2, and self-made 1% Pt/CNTs, were very similar (Figure 8a and Supporting Information): In the beginning of the reaction, the nitro group was converted almost exclusively to the amine and intermediate hydrogenation products (i.e., mostly the hydroxylamine). When the substrate was fully converted, hydrogenation of the double bond commenced with a comparable reaction rate, resulting in the undesired overhydrogenated product. This behavior is different from that observed with Pt-Q@IL/CNTs, where the double bond was virtually only hydrogenated (with a low rate) after both the substrate and the intermediate hydrogenation products had been converted. In contrast, the behaviors of the catalysts in the presence of small amounts of [BMIM][FEP] were different from each other (Figure 9). With 5% Pt/C, the reaction pathway in the presence of IL was similar to that of the unmodified catalyst; i.e., the reaction proceeded smoothly to EA, achieving only a low intermediate selectivity
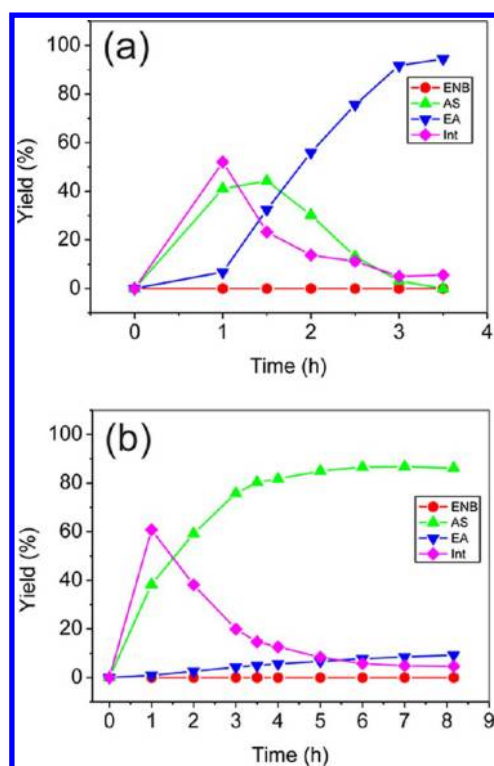
Figure 8. Reaction pathway in the hydrogenation of NS with 1% Pt/CNT under basic conditions without (a) and with (b) IL. Conditions: NS:Pt = 500:1 (mol/mol), NEt₃ (NS concentration 0.47 mmol/mL), dodecane as internal standard, optional addition of 30 mg of [BMIm][FEP]/100 mg of CNTs, 1 bar of H₂, rt.
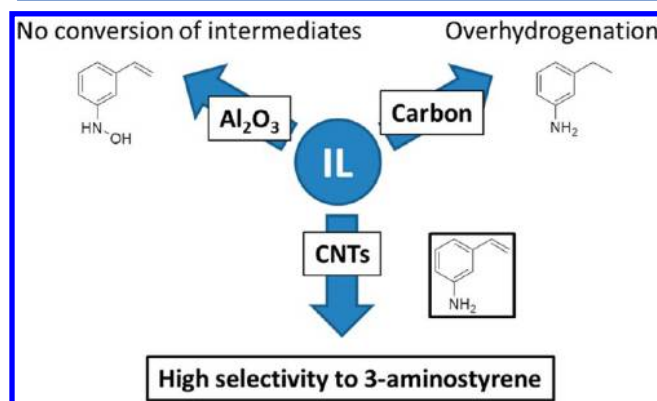
Figure 9. Effect of IL on the hydrogenation of NS over Pt supported on Al₂O₃, carbon, and CNTs.

for AS (see the Supporting Information). The effect of the IL was overall small and mainly caused the intermediate hydrogenation products to be converted somewhat slower.

With 5% Pt/Al₂O₃ as a catalyst, the IL had a strong effect. While modified 5% Pt/Al₂O₃ still smoothly converted NS (though with a lower rate), the presence of the IL almost completely suppressed the hydrogenation of both the intermediates and AS (see the Supporting Information), also under more forcing conditions. Hence, while the presence of the IL strongly modified the reaction pathway, no beneficial effect on the AS selectivity was obtained.

This was different when CNTs were used as a support (Figure 8b). Here, the effect on the catalyst was also strong but additionally gave rise to much higher selectivities for the desired

AS. Further hydrogenation of AS was effectively suppressed, resulting in a maximum yield of 87%, i.e., around 40% more than in the case without IL.

■ DISCUSSION

By applying costabilizers in addition to the IL during the synthesis of Pt NPs, the size of the NPs could be decreased from 3.4 to less than 2 nm and also the selectivity in the hydrogenation to ENB could be improved from around 60% to 80%. As in previous studies in the selective hydrogenation of NS (though targeting AS), obtaining high selectivities requires proper catalyst design.

However, it was found that the selectivity could also be controlled to a high degree by adjusting the crucial reaction parameters. In comparison to other approaches, this resulted in more active catalysts. The key parameter for directing the selectivity was the use of an acid or a base. Noticeably, with the same catalyst, hydrogenation of the C=C bond under acidic conditions or the NO₂ group under basic conditions (to a mixture of NO₂ hydrogenated products) with a specific selectivity higher than 90% could be obtained. On the contrary, parameters such as temperature and pressure had significantly less influence on the selectivity, but gave access to higher reaction rates. To the best of our knowledge the possibility to control the selectivity in the hydrogenation of NS or similar molecules by a simple solvent-controlled acid–base switch has not yet been reported. A beneficial effect of a combination of both acidic and basic sites (i.e., both present simultaneously) of the catalyst support has previously been discussed.[29]

The preferential hydrogenation of the nitro group under basic conditions might be explained by the known preferential adsorption of nitrobenzene on basic sites, which is exploited for determining their number on solid catalysts.[44] Thus, the preferential hydrogenation of the nitro group is likely occurring on basic sites created by triethylamine, which adsorbs readily on Pt.[45]

The hydrogenation of the nitro group under basic conditions with the purely IL-supported Pt NPs afforded a mixture of products, constituting AS and (mainly) 3-(*N*-hydroxylamino)-styrene. The latter was barely further converted over the Pt NPs in IL. This behavior is greatly different from that of the IL-free more commonly used solid catalysts (e.g., Pt/Al₂O₃), where 3-(*N*-hydroxylamino)styrene was indeed hydrogenated smoothly, but since also EA formed in considerable amounts, the selectivity for AS remained poor.

Between these two scenarios—(1) no hydrogenation of intermediate products and (2) overhydrogenation to EA—the immobilization of Pt NPs in IL on CNTs resulted in a third scenario: the intermediates were hydrogenated smoothly to AS without generation of EA in high amounts. Comparative experiments with Pt/CNTs (synthesized without IL) showed the tremendous effect of the IL on this system. In the absence of IL, Pt/CNTs resulted in the formation of overhydrogenated products (which would resemble scenario 2), while the IL as an additive strongly modified the reaction pathway to give AS in high yields. Compared to other approaches described in the literature relying on partially blocking the catalyst surface, the catalyst already exhibits significant activity at 1 bar of H₂ and rt. ILs can adsorb on Pt and therefore modify its catalytic performance in hydrogenation reactions.[38] It can be speculated that the adsorption behavior of the IL on the catalyst depends on the type of the support (here CNTs), and this suppresses

C═C adsorption and hydrogenation while still allowing adsorption and hydrogenation of 3-(N-hydroxylamino)styrene.

CONCLUSIONS

Platinum nanoparticles in the size range of 1.7−3.4 nm were synthesized in an IL ([BMIM][FEP]) for use in the chemoselective hydrogenation of 3-nitrostyrene. The presence of the IL, the reaction medium (acidic or basic), and the type of support greatly influence the catalytic properties of the Pt nanoparticles. The selectivity for either C═C or NO$_2$ group hydrogenation could be controlled by either basic or acidic conditions. Yields above 90% of 3-ethylnitrobenzene were achieved using trifluoroacetic acid as an additive. Under basic conditions, the nitro group was preferentially hydrogenated to give a mixture of mainly 3-aminostyrene and 3-(N-hydroxylamino)styrene, the latter in succession being responsible for the formation of undesired overhydrogenation products. The yields of 3-aminostyrene could be increased by ca. 40% to around 90% by depositing the Pt NPs on carbon nanotubes. Comparative experiments with IL-free catalysts revealed that the presence of the IL was mandatory to achieve high selectivities for 3-aminostyrene. The synthesized catalysts were catalytically active at rt under 1 bar of H$_2$ and showed no sign of deactivation upon reuse.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Hydrogenation pretests with Pt@IL and Pt/Al$_2$O$_3$, Pt NP sizes obtained from TEM, variation of the substrate-to-catalyst ratio for vinylic hydrogenation, solvent variation, influence of temperature and pressure, influence of mass transport, and selective hydrogenation using conventional catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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