

Synthesis of Bipyridine-Stabilized Rhodium Nanoparticles in Non-Aqueous Ionic Liquids: A New Efficient Approach for Arene Hydrogenation with Nanocatalysts

Bastien Léger,^a Audrey Denicourt-Nowicki,^a Alain Roucoux,^{a,*}
and Hélène Olivier-Bourbigou^b

^a Equipe Synthèse Organique et Systèmes Organisés, UMR CNRS 6226 “Sciences Chimiques de Rennes”, Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Gal Leclerc, 35700 Rennes, France

Fax: (+33)-(0)-2-2323-8199; e-mail: Alain.Roucoux@ensc-rennes.fr

^b IFPLyon, BP3, 69390 Vernaison, France

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Abstract: A new approach to stabilize metal nanoparticles with polynitrogen ligands in ionic liquids (ILs) is described. Zerovalent metal nanospecies in the size range of 2.0 nm were easily prepared in various ionic liquids by chemical reduction of a rhodium salt with an excess amount of sodium borohydride (NaBH_4) and efficiently stabilized by 2,2'-bipyridine. The influence of the bipyridine ratio in various ILs

according to the nature of the cation-anion association was investigated. These nanocatalysts were evaluated in the hydrogenation of aromatic compounds in ILs under various catalytic conditions ($P=1-40$ bar, $T=20-80^{\circ}\text{C}$).

Keywords: arenes; biphasic catalysis; hydrogenation; ionic liquids; nanoparticles; rhodium

Introduction

The recent period has evidenced an ever-increasing interest in the controlled synthesis of nanometer-sized metal species, namely metal nanoparticles or colloids, and their application in various areas such as catalysis.^[1,2] The development of soluble species as highly active nanocatalysts has been the focus of considerable effort and several groups have significantly contributed to this central field.^[3–5] The main advantage of nanospecies in catalysis is related to their small size leading to high surface/volume ratios and consequently high numbers of potential active sites. Nowadays, soluble noble metal nanoparticles are considered as an indispensable family of catalysts at the border between homogeneous and heterogeneous chemistry.^[6]

These metal nanocatalysts can be synthesized by various methods according to the “organic” or “aqueous” nature of the media, the nature of the precursor and, finally, the type of the used stabilizers.^[7,8] Therefore, various protecting agents, such as polymers, surfactants, ligands, cyclodextrins but also dendrimers and ionic liquids, have been used. Today, among these various stabilizers, ligands displaying steric stabilization are strategically considered due to the border with a homogeneous approach. The use of ligands allows particle entrapment by strong interactions, in

particular with coordination onto the surface of the particles, thus having a potential direct influence on catalytic activity or selectivity. For example, N-donor compounds have already proved to be efficient protective agents for metallic nanoparticles.^[9–11] Among conventional organic solvents used, ionic liquids (ILs) have shown to have significant advantages in terms of activity, selectivity and reusability in catalysis.^[12,13] Moreover, several nanometallic catalysts have been reported to be activated in ionic liquids. Therefore, Dupont and co-workers^[14–18] have described the synthesis of nanoparticles of various noble metals stabilized into different ionic liquids such as [BMI][PF₆] (BMI = 1-butyl-3-methylimidazolium) for the biphasic hydrogenations of alkenes and arenes. However, in some cases, imidazolium-based ILs present limitations in nanoparticle stabilization, leading to a precipitation step before solventless, solution or redispersed use, respectively, as heterogeneous or homogeneous catalysts or in a biphasic system.^[19]

In this paper, we report a new approach based on the use of ligands as stabilizing agent of nanoparticles in ionic liquids for the catalytic hydrogenation of arenes in biphasic conditions. The ability of N-donor ligands to induce a stabilization has previously been described by Han and co-workers in the case of phenanthroline as a protective agent of palladium nanoparticles for olefin hydrogenation in [BMI][PF₆]

media.^[20] Here, we describe the synthesis of zerovalent rhodium nanoparticles and their efficient stabilization with 2,2'-bipyridine (Bipy) as a polynitrogen ligand. We combine different stabilizing effects leading to more stable catalytic systems and to potential selectivities. After optimization of the Rh/Bipy ratios, the catalytic system has been studied in the hydrogenation of styrene, possessing an easily reducible exo-C=C double bond and an aromatic ring. This strategy has been investigated in various non-aqueous ILs according to the nature of the anion and cation fragments. Finally, the best 2,2'-bipyridine-stabilized Rh system has been evaluated in the hydrogenation of various arene derivatives. This catalytic reaction represents an important industrial transformation, in particular with the conversion of benzene into cyclohexane or cyclohexene, a key intermediate in adipic acid synthesis,^[21] and also for actual environmental constraints.^[22]

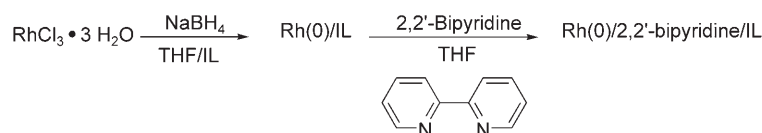
Results and Discussion

The catalytically active suspensions consist of metallic rhodium(0) nanoparticles prepared by reducing rhodium trichloride with sodium borohydride in a monophasic tetrahydrofuran-ionic liquid media. The stabilizing agent 2,2'-bipyridine, dissolved in THF, is added to the pre-stabilized-metallic rhodium(0) immediately after reduction, according to the procedure described in Scheme 1. In this protocol, we consider a preliminary stabilization due to a weak interaction from the

ionic liquid^[14–18] and/or THF^[23] onto the outer shell of the nanoparticles, followed by a stronger stabilization through the coordination of 2,2'-bipyridine. This strategy uses the recognized controlling role of ionic liquids or THF during the growth step and finally to limit the nanoparticle aggregation phenomenon.

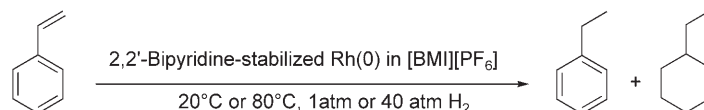
The so obtained catalytic systems have been tested in the hydrogenation reaction of aromatic derivatives. The optimization of the reaction conditions (temperature, hydrogen pressure, bipyridine ratio) has been performed with styrene as a model substrate. First, we have investigated the best hydrogenation conditions, using bipyridine-stabilized Rh(0) nanoparticles in [BMI][PF₆] [bipyridine/Rh(0)=0.5]. The results are summarized in Table 1.

In all cases, the colloidal suspension is stable after catalytic reaction. Under mild conditions (entry 1), no hydrogenation of the aromatic ring is observed. An increase of the hydrogen pressure up to 40 bar has no significant effect on the catalytic activity (entry 2), whereas an increase of both the temperature and the hydrogen pressure (entry 3) leads to the hydrogenation of the aromatic ring. Thus, all the following hydrogenation reactions will be carried out under these standard conditions (80 °C, 40 bar H₂). The reduction method for the nanoparticles synthesis has also been studied to check the potential influence of boron species in the media. Rhodium(0) colloids have been prepared using molecular H₂ as reducing agent. Finally, no dramatic effects in term of catalytic activity have been observed (entries 3 and 4), showing that potential boron impurities in the media or onto the nano-



Scheme 1. Synthesis of rhodium(0) nanoparticles in ionic liquids.

Table 1. Optimization of styrene hydrogenation with 2,2'-Bipy-stabilized Rh(0) nanoparticles in [BMI][PF₆].^[a]



| Entry | T [°C] | P _{H₂} [Atm] | Product | Selectivity [%] ^[b] | Time [h] |
|------------------|--------|----------------------------------|-------------------------------|--------------------------------|----------|
| 1 | 20 | 1 | ethylbenzene | 100 | 3 |
| 2 | 20 | 40 | ethylbenzene/ethylcyclohexane | 95/5 | 15 |
| 3 | 80 | 40 | ethylbenzene/ethylcyclohexane | 40/60 | 15 |
| 4 ^[c] | 80 | 40 | ethylbenzene/ethylcyclohexane | 45/55 | 15 |

^[a] Reaction conditions: Rh (3.8 × 10⁻⁵ mol), ligand (1.9 × 10⁻⁵ mol), [BMI][PF₆] (2 mL), substrate/Rh = 100 (molar ratio), stirred at 1500 rpm.

^[b] Determined by GC analysis, styrene is totally converted

^[c] Reduction step performed under 40 bar H₂ in THF/ionic liquid.

particles surface have no significant poisoning behaviour.

Then, the ligand ratio has been studied in terms of stability of the colloidal suspension and catalytic activity under standard hydrogenation conditions after 15 h of reaction. Table 2 shows the obtained results.

First, interesting results in terms of catalytic activity are obtained with [Bipy]/[Rh] ratio from 0 to 0.4 (entries 1–3) with complete conversion of styrene into ethylcyclohexane. Unfortunately, with such molar ratios, the colloidal suspensions are unstable after catalytic reactions, leading to the formation of aggregates. These experiments justify the use of bipyridine as a stabilizing agent for the nanoparticles. Moreover, an increase of [Bipy]/[Rh(0)] ratio up to 0.75 decreases the catalytic activity, probably due to a surface hindrance which limits the access of the substrate to the metallic active sites (entry 5). Thus, a molar [Bipy]/[Rh(0)] ratio of 0.5 seems to be a good compromise between stability and catalytic activity.

The previously optimized 2,2'-bipyridine-stabilized rhodium(0) nanoparticles in [BMI][PF₆] have been characterized by transmission electron microscopy

(TEM). These observations show that the particles are organized in spherical superstructures. However, in some regions, well-dispersed particles have been observed. In both cases, the nanoparticles have an average diameter of 2.0 nm as shown on the size histogram which results from the measurement of about 155 particles. These observations are in agreement with those obtained for ionic liquid-stabilized colloids and reported by Dupont.^[17] Finally, it seems that 2,2'-bipyridine has no real and significant influence on the particle size and structural organization. Figure 1 shows the mono-modal size distribution of 2,2'-Bipy-stabilized Rh(0) nanoparticles in [BMI][PF₆]. For a standard ratio [2,2'-Bipy]/Rh of 0.5, very stable suspensions are obtained without any agglomeration during several months. They can be stored in air without special precautions.

The influence of ionic liquids has also been investigated, using different cations and anions. Indeed, Dyson and co-workers have also reported a study concerning the effects of cationic heads and anions for carbon-carbon coupling reactions.^[24–26] First, different anions in association with the same cation [BMI]

Table 2. Influence of the ligand ratio on catalytic activity.^[a]

| Entry | [Bipy]/[M] ratio | Product | Selectivity [%] ^[b] |
|-------|------------------|-------------------------------|--------------------------------|
| 1 | 0 | ethylcyclohexane | 100 |
| 2 | 0.2 | ethylcyclohexane | 100 |
| 3 | 0.4 | ethylbenzene/ethylcyclohexane | 5/95 |
| 4 | 0.5 | ethylbenzene/ethylcyclohexane | 40/60 |
| 5 | 0.75 | ethylbenzene/ethylcyclohexane | 77/23 |

^[a] Reaction conditions: Rh (3.8×10^{-5} mol), [BMI][PF₆] (2 mL), substrate/Rh = 100 (molar ratio), 40 atm H₂, 80 °C, 15 h, stirred at 1500 rpm.

^[b] Determined by GC analysis, styrene is totally converted.

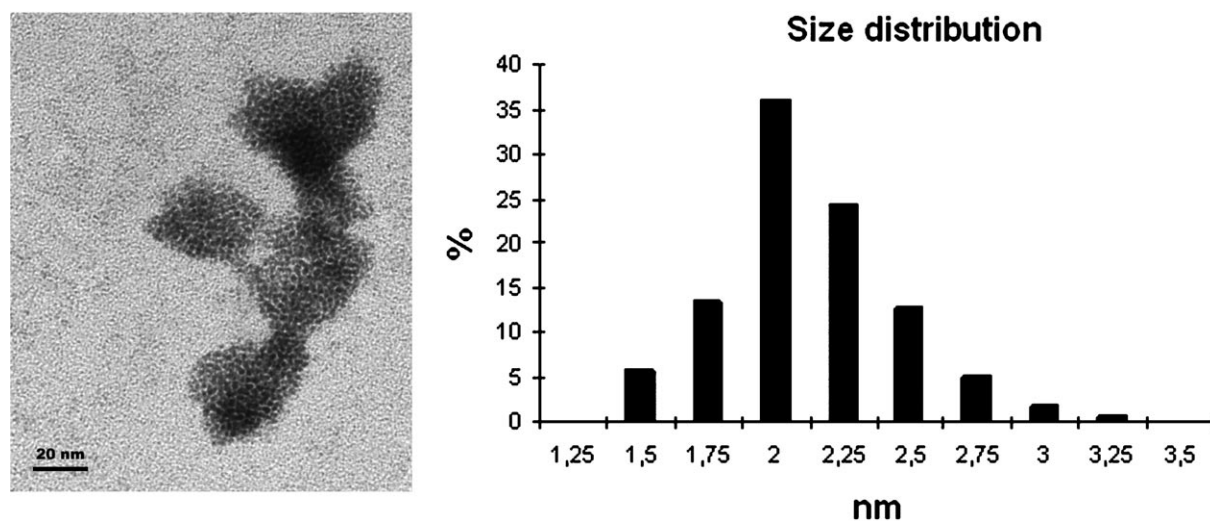


Figure 1. TEM micrograph (left) and size distribution (right) of 2,2'-bipyridine-stabilized Rh(0) nanoparticles into [BMI][PF₆] (scale bar = 20 nm).

have been studied and the results are summarized in Table 3.

The anion has a great influence on the catalytic activity. In all cases, the bipyridine-stabilized rhodium(0) suspensions are stable after catalytic reaction. However, in terms of catalytic activity and selectivity, the best results are obtained with [BMI][BF₄] with a quasi total conversion of styrene into ethylcyclohexane (entry 2). On the other hand, in the case of [BMI][N(CN)₂] (entry 4), styrene is completely converted into ethylbenzene and no hydrogenation of the aromatic ring is observed. Undoubtedly, the coordination ability of the anion towards the metallic species influences the activity, as previously reported.^[25,27] Indeed, the use of strongly coordinating anions tends to inhibit the catalytic activity. This phenomenon was also confirmed by a supplementary experiment based on the use of the acetate anion [CH₃CO₂][−], which is known to be strongly coordinating. Under 40 atm of H₂ and at room temperature, styrene was completely converted into ethylbenzene in [BMI][CH₃CO₂]. No aromatic ring hydrogenation was observed due to an efficient coordination of the anion onto the active sites.

Secondly, different cations associated with the same anion [NTf₂ = bis(trifluoromethanesulfonyl)imide anion] have also been investigated. The NTf₂ anion

was chosen so that the ionic liquids could be easily and rapidly prepared and could be liquid at ambient temperature. In particular, ionic liquids based on heterocyclic skeletons such as imidazolium (BMI = 1-*n*-butyl-3-methylimidazolium), pyrrolidinium (MBPyr = *N*-methyl-*N*-butylpyrrolidinium) and pyridinium (MBPyr = 1-butyl-4-methylpyridinium) rings have been used as solvents in our model catalytic reaction. These two last cations have been tested in order to avoid the potential formation of carbenes, as it has already been demonstrated with BMI.^[28,29] Finally, we have also evaluated a classical ammonium salt such as the *N,N*-dimethyl-*N*-dodecyl-*N*-(2-hydroxyethyl)ammonium group (HEA) in opposition to heterocyclic compounds. The synthesis of [HEA][NTf₂] was performed according to a procedure developed in our laboratory.^[30] The results concerning the influence of the cations are presented in Table 4.

In all cases, the 2,2'-Bipy-protected Rh(0) colloidal suspensions are stable after reaction and are active in the hydrogenation of arene compounds. Similar results are obtained with imidazolium and pyrrolidinium cations (entries 1 and 4). However, the best activity for aromatic hydrogenation was obtained in [HEA][NTf₂] with an ethylbenzene/ethylcyclohexane ratio of 40/60. As the nanoparticles are always stable after 15 h of reaction, we could presume the complete con-

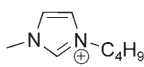
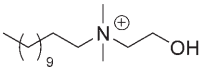

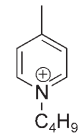
Table 3. Influence of the anion of the ionic liquid on catalytic activity.^[a]

| Entry | Ionic liquid | Product | Selectivity [%] ^[b] |
|-------|----------------------------|-------------------------------|--------------------------------|
| 1 | [BMI][PF ₆] | ethylbenzene/ethylcyclohexane | 40/60 |
| 2 | [BMI][BF ₄] | ethylbenzene/ethylcyclohexane | 8/92 |
| 3 | [BMI][NTf ₂] | ethylbenzene/ethylcyclohexane | 70/30 |
| 4 | [BMI][N(CN) ₂] | ethylbenzene | 100 |

^[a] Reaction conditions: Rh (3.8 × 10^{−5} mol), ligand (1.9 × 10^{−5} mol), ionic liquid (2 mL), substrate/Rh = 100 (molar ratio), 40 atm H₂, 80 °C, 15 h, stirred at 1500 rpm.

^[b] Determined by GC analysis, styrene is totally converted

Table 4. Influence of the cation on catalytic activity.^[a]

| <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>BMI</p> </div> <div style="text-align: center;">  <p>HEA</p> </div> <div style="text-align: center;">  <p>MBPyr</p> </div> <div style="text-align: center;">  <p>MBPyr</p> </div> </div> | | | |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|-------------------------------|--------------------------------|
| Entry | Ionic liquid | Product | Selectivity [%] ^[b] |
| 1 | [BMI][NTf ₂] | ethylbenzene/ethylcyclohexane | 70/30 |
| 2 | [HEA][NTf ₂] | ethylbenzene/ethylcyclohexane | 40/60 |
| 3 | [MBPyr][NTf ₂] | ethylbenzene/ethylcyclohexane | 85/15 |
| 4 | [MBPyr][NTf ₂] | ethylbenzene/ethylcyclohexane | 70/30 |

^[a] Reaction conditions: Rh (3.8 × 10^{−5} mol), ligand (1.9 × 10^{−5} mol), ionic liquid (2 mL), substrate/Rh = 100 (molar ratio), 40 atm H₂, 80 °C, 15 h, stirred at 1500 rpm.

^[b] Determined by GC analysis. Styrene was totally converted.

Table 5. Hydrogenation of substituted aromatic compounds by 2,2'-Bipy-stabilized Rh(0) nanoparticles in [BMI][PF₆].^[a]

| Entry | Substrate | Conversion [%] ^[b] | Product obtained |
|-------|---------------|-------------------------------|---------------------------------------|
| 1 | benzene | 100 | cyclohexane |
| 2 | ethylbenzene | 60 | ethylcyclohexane |
| 3 | propylbenzene | 85 | propylcyclohexane |
| 4 | cumene | 10 | iso-propylcyclohexane |
| 5 | styrene | 100 | ethylbenzene/ethylcyclohexane (40/60) |
| 6 | toluene | 100 | methylcyclohexane |

^[a] Reaction conditions: Rh (3.8×10^{-5} mol), ligand (1.9×10^{-5} mol), [BMI][PF₆] (2 mL), substrate/Rh = 100 (molar ratio), 40 atm H₂, 80 °C, 15 h, stirred at 1500 rpm.

^[b] Determined by GC analysis.

version of styrene into ethylcyclohexane for longer reaction times.

After optimization of the various reaction parameters, we have investigated the hydrogenation of various aromatic derivatives, using 2,2'-Bipy-stabilized rhodium(0) nanoparticles in [BMI][PF₆] (Table 5).

The 2,2'-bipyridine-stabilized Rh(0) nanoparticles in [BMI][PF₆] are efficient catalysts for the hydrogenation reaction of various aromatic compounds. However, it seems that the presence of bulkier substituents on the aromatic ring tends to decrease the catalytic activity. This phenomenon has already been reported in various media.^[6,31] It could be explained by the fact that increasing steric hindrance of aromatic compounds tends to limit the access to the nanoparticles surface by a stronger interaction between substrate and bipyridine.^[32] Finally, the potential recycling process and the catalytic lifetime of the suspension were also studied. A successive hydrogenation of styrene was carried out with the 2,2'-bipyridine stabilized nanoparticles in ionic liquids. No loss of activity was observed during the second run justifying the stability of bipyridine rhodium nanoparticles system and finally this investigated approach.

Conclusions

To conclude, we have developed a new approach to stabilize nanoparticles in ionic liquids, using 2,2'-bipyridine as a protecting agent. We have showed that 2,2'-bipyridine has no significant influence on the nanoparticles organization and size but it brings an efficient stabilizing effect in catalytic reactions. Metal nanoparticles in a size range of 2.0 nm have been easily prepared in different various ionic liquids with a reproducible and direct method, which does not need treatments such as precipitation before use. These nanocatalysts have shown interesting activities and selectivities in the hydrogenation of substituted aromatic compounds. We have demonstrated that the bipyridine ratio and the cation-anion association of the ionic liquids have a great influence on the selec-

tivity of the reaction. Finally, the colloidal suspension could be easily recycled and reused for successive hydrogenations.

Experimental Section

General Procedures

All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen in oven-dried glassware. THF was distilled from sodium/benzophenone. Rhodium chloride hydrate was obtained from Strem Chemicals. Sodium borohydride, 2,2'-bipyridine and all arenes were purchased from Aldrich or Acros and were used without further purification. Water was distilled twice before use by conventional methods. The [BMI][BF₄] ionic liquid was purchased from Solvionic and the other ionic liquids were prepared following already described procedures.^[33–38] The [BMI][PF₆] ionic liquid was prepared according to a known procedure,^[39] dried under vigorous stirring during 6 h, at 70 °C and under vacuum. Its chloride content was checked by the AgNO₃ test and purity by ¹H and ³¹P NMR spectra.

Analytical Procedures

TEM Analysis: The transmission electronic microscopic studies were conducted using an FEI Technai G2 Sphera at 200 kV (cathode LaB6). Samples were prepared by a dropwise addition of the stabilized rhodium nanoparticles in ionic liquids onto a copper sample mesh covered with carbon. The colloidal suspension was partially removed after 1 min using cellulose before transferring to the microscope. The picture is obtained at $\times 80,000$ with a video GATAN USC1000 (CCD detector 2048 \times 2048) and associated software DIGITAL Micrograph. Measurement of about 155 particles was made with program SCION Image (NIH) and analyzed with the Excel® program providing the histograms of the nanoparticles size distribution.

Gas Chromatography: All analysis were performed using Carlo Erba GC 6000 with FID detector equipped with an AltechAT1 column (30 m, 0.25 mm i.d.). Parameters were as follows: temperature, 80 °C ; injector temperature, 220 °C ; detector temperature, 250 °C.

Synthesis of the Rhodium(0) Suspension

The colloidal suspension was prepared at ambient temperature and at open air. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (10 mg, 3.8×10^{-5} mol) was dispersed in a mixture of THF (5 mL) and $[\text{BMI}][\text{PF}_6]$ (2 mL). NaBH_4 (3.6 mg, 9.5×10^{-5} mol, 2.5 equivs.) dissolved in water (2 drops) was quickly added to the mixture under vigorous stirring. Immediately, 2,2'-bipyridine (2.9 mg, 1.9×10^{-5} mol, 0.5 equiv./Rh) dissolved in 5 mL of THF was quickly added under vigorous stirring to mixture. Then, THF was eliminated under reduced pressure and the colloidal suspension was dried under vacuum during 2 h. The reduction occurs instantaneously and is characterized by a colour change from red to black. The obtained suspensions are stable for several weeks. A similar reduction procedure has been carried out with molecular hydrogen as reducing agent. Nanoparticle synthesis was performed under 40 bar H_2 during 40 mn, followed by a stabilization step with addition of 2,2'-bipyridine.

General Procedure for Hydrogenation under Hydrogen Pressure

The stainless steel autoclave was charged with 2 mL of bipyridine-stabilized Rh(0) colloidal suspension in $[\text{BMI}][\text{PF}_6]$ and a magnetic stirrer. The appropriate substrate (3.8×10^{-5} mol, 100 equivs.) was added into the autoclave and dihydrogen was admitted to the system at constant pressure up to 40 atm. The mixture was heated to 80 °C and stirred during 15 h. After cooling to ambient temperature, the mixture was dispersed into 10 mL of CH_3CN and centrifuged ($g = 20152 \text{ ms}^{-2}$) during 10 min for the precipitation of nanoparticles. The sample was analyzed by gas chromatography.

For the recycling procedure, after 15 h of reaction and after cooling back to ambient temperature, the products were extracted by liquid-liquid extraction and decantation with diethyl ether until complete elimination of organic products from the ionic liquid phase. After drying, the colloidal suspension was reused in a second hydrogenation in the cleaned autoclave.

Acknowledgements

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