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PAPER

Influence of amines on the size control of *in situ* synthesized ruthenium nanoparticles in imidazolium ionic liquids

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Very stable suspensions of small sized (*c.a.* 1.2 nm) and homogeneously dispersed ruthenium nanoparticles (RuNPs) were obtained by decomposition, under H_2, of (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium(0), [Ru(COD)(COT)], in various imidazolium derived ionic liquids (ILs: [RMIm][NTf_2] (R = C_nH_{2n+1} where $n = 2; 4; 6; 8; 10$) and in the presence of amines as ligands (1-octylamine, 1-hexadecylamine). These nanoparticles were compared to others stabilized either in pure ILs or by the same ligands in THF. NMR experiments (^{13}C solution and DOSY) demonstrate that the amines are coordinated to the surface of the RuNPs. These RuNPs were investigated for the hydrogenation of aromatics and have shown a high level of recyclability (up to 10 cycles) with neither loss of activity nor significant agglomeration.

1. Introduction

The use of metal nanoparticles (MNPs) as catalysts is a topic of growing interest at the frontier between homogeneous and heterogeneous catalysis.[1,2] While homogeneous catalysts are generally difficult to extract from the reaction products, but highly efficient and selective, heterogeneous ones are easily separated from the reaction mixtures and are generally not altered by high reaction temperatures.[3] This is probably the main reason why heterogeneous catalysis has been very successful so far. The development of nanocatalysts is expected to overcome the disadvantages of both kinds of catalysts while keeping their advantages. As the activity and selectivity of metal nanoparticles are dependent on their size and shape, it is of primary importance to control these parameters.[4–7]

Several stabilization methods are known to be effective at obtaining stable MNPs, such as the use of polymers, ligands and organic or inorganic templates.[1,6] In this area, a general procedure for the synthesis of MNPs in organic solvents, by the reduction of organometallic complexes under dihydrogen in the presence of various ligands such as alcohols, phosphines or amines as stabilizers has been developed. This approach affords MNPs with narrow size distributions, but the size of these particles can not be predicted. Nevertheless, comparative studies have shown that ligands can be classified into two main categories—weak and strong ligands.[8] Strong ligands such as thiols and phosphines,[9,10] tend to favour the formation of small MNPs with very narrow size-distributions, while weak ligands such as amines lead to larger size distributions and allow the growth of the particles.[11] However, the presence of appropriate ligands can lead to selective catalysts.[12]

Besides classical modes of stabilization for MNPs, the use of ionic liquids (ILs) is emerging as an environmentally friendly alternative for NP synthesis.[13] ILs play a double role, acting as both the solvent and the stabilizer.[14,15]

Currently, ILs are defined as "supramolecular" fluids due to their extended hydrogen-bond networks.[16] In addition to this H-bond network, there is a continuous tridimensional network of ionic channels, coexisting with the non-polar domains which form, in some cases, dispersed microphases ($n = 2$) or, in others, continuous ones ($n = 12$). From literature data, both experiments and simulations have shown that the side-chain length has a strong influence on the size of the non-polar domains of ILs. In addition, X-ray diffraction (XRD) experiments proved that, in [RMIm][Cl], (R = C_nH_{2n+1}), the size of non-polar domains increases from 13 to 27 Å when n varies from 3 to 10.[17–20] The segregation of polar and non-polar domains in imidazolium-based ILs has a strong influence on their solvation and their ability to interact with different species. Indeed, polar substrates are preferentially dissolved in polar domains and non-polar compounds in non-polar ones. The two extreme situations are those such as hexane and water solutions where the solute is concentrated either in the non-polar domain or in the charged domain.[18,21]

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Recently, a relationship between the size of these non-polar domains and the size of RuNPs prepared *in situ* from the organometallic complex (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium(0), [Ru(COD)(COT)], has been found.[22] This suggests that the phenomenon of crystal growth is probably controlled by the local concentration of [Ru(COD)(COT)] and consequently, limited to the size of these non-polar domains. Ionic liquids can be considered to be organized systems that are formed *via* a self-assembly process and resemble nano-reactors in which the size of RuNPs can be controlled.

However, under standard experimental catalytic conditions (temperature, stirring, or carbon monoxide atmosphere) the RuNPs in ILs have not been found to be stable towards agglomeration and coalescence.[23] In order to develop new catalytic systems based on stable and size-controlled NPs in ILs we combined two approaches, namely the control of the local concentration of [Ru(COD)(COT)] into the non-polar domains of ILs[22] and the use of ligands to increase NP stability.[8,24–27]

In this paper, we describe the synthesis of RuNPs by decomposition, under H_2, of the organometallic precursor [Ru(COD)(COT)] in mild conditions (3 bar H_2, 30 °C) and in several ILs 1-alkyl-3-methyl-imidazoliumbis(trifluoromethanesulfonyl)imide [C_1C_nIm]][NTf_2], (C_n = butyl, hexyl, octyl, decyl), in the presence of amines as stabilizing ligands (1-octylamine, 1-hexadecylamine). The resulting colloidal suspensions have been investigated for the catalytic hydrogenation of toluene.

2. Results and discussion

2.1 Synthesis and characterization of ruthenium nanoparticles

Decomposition of [Ru(COD)(COT)], by dihydrogen is a well-known method for synthesizing RuNPs in organic solvents.[8,27] The same procedure has been successfully applied to the synthesis of RuNPs in pure imidazolium ionic liquids.[22,28–30] Here we report the synthesis of RuNPs in different ILs and in the presence of amines added to the reaction medium as stabilizing ligands, as shown in Scheme 1.

The ILs used in this work are: 1-alkyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide [C_1C_nImNTf_2], (C_n = butyl, hexyl, octyl, decyl) and the ligands: 1-octylamine ($C_8H_{17}NH_2$) and 1-hexadecylamine ($C_{16}H_{33}NH_2$). Octylamine and hexadecylamine have previously been described as effective agents for the stabilization of RuNPs in tetrahydrofuran (THF) as solvent.[8] The increase in the stability of metal NPs in ILs, by addition of an extra ligand has already been reported,[15] however to the best of our knowledge, they have not been used in the *in situ* synthesis of nanoparticles in ILs.

In a Fischer–Porter reactor, the metal source [Ru(COD)(COT)] (0.21 mmol), and the chosen ligand ([RNH_2]/[Ru(COD)(COT)] = 0.2), were dispersed in the IL (5 mL). The reaction mixture was then set to 30 °C, stirred for 2 h, and then pressurized with a H_2 atmosphere (3 bar). After 20 h of vigorous stirring, the remaining hydrogen and cyclooctane (COA; a by-product of the reaction resulting from the metal precursor reduction) were eliminated under vacuum. The black colloidal suspensions obtained were stored under argon at room temperature. These colloidal suspensions remained stable for long periods of time, as checked by transmission electron microscopy (TEM) in ILs, showing neither precipitation nor aggregation after more than 9 months under argon. Selected TEM micrographs with corresponding size histograms are presented in Fig. 1a–f. The different colloidal systems obtained in this way are described in Table 1.

The RuNPs are well dispersed on the TEM grids and no agglomeration was observed. In addition, they display an almost spherical shape and are of similar sizes that are between the limits of error, in the range 1.1–1.3 nm, whatever the IL or the ligand used for their synthesis (Table 1).

The nanoparticles obtained in the presence of octylamine have also been characterized by high resolution electron microscopy (HRTEM) in ILs (Fig. 2). The high resolution results have been used to check the crystalline structure of the nano-particles. Fourier (FFT) analyses performed on the high resolution images (see Fig. 2c) confirm that the particles have the same hexagonal structure as bulk ruthenium if the experimental errors (a 5% error on the calibration of the magnification has been considered) are taken into account. In addition, the measured distances and angles are compatible (within a 5% error) with the hexagonal structure of bulk ruthenium showing that the particle is oriented in a [2, −1, −1, 3] zone axis (see Fig. 3).

The characteristics of these RuNPs can be compared with those of previously obtained RuNPs synthesized with the same ligands in an organic solvent (THF),[8] as well as in the same-but-ligandless ILs.[22,28–30]

First of all, the synthesis was carried out in THF in the presence of octylamine in the same molar ratio as reported above, *i.e.* [$C_8H_{17}NH_2$]/[Ru(COD)(COT)] = 0.2, which gives rise to spherical RuNPs with a mean size of 2.3 nm which are agglomerated into spherical superstructures of approximately 100 nm. In the same reaction conditions, but with hexadecylamine as stabilizer, elongated RuNPs of a mean size of 1.9 nm were observed, both of which are larger than the RuNPs formed by the new method which display a mean diameter of around 1.2 nm. In addition,

$$\mathbf{Ru(COD)(COT) + IL + RNH_2 \xrightarrow[30°C;\ 20h;\ stirring]{H_2\ (3\ bar)} RuNPs/RNH_2/IL + COA}$$

IL = 1-alkyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide [C_1C_nImNTf2],
(Cn = butyl, hexyl, octyl, decyl)
$RNH_2 = C_8H_{17}NH_2$; $C_{16}H_{33}NH_2$
[RNH_2]/[Ru(COD)(COT)]=0.2   COA = cyclooctane

Scheme 1 *In situ* synthesis of RuNPs in an IL and in the presence of amines as stabilizers.

Table 1 Mean sizes of Ru NPs, depending on the nature of the ligand and of the ILs [C_1C_nImNTf$_2$]

Entry	IL	Ligand[a]	Average diameter (nm)	[L]/[Ru_S][b]	Colloid
1	C_1C_4ImNTf$_2$	hexadecylamine	1.3 (0.4)	0.27	*C4·HDA*
2	C_1C_4ImNTf$_2$	octylamine, no stirring	1.2 (0.4)	0.26	*C4·OA·NS*
3	C_1C_4ImNTf$_2$	octylamine	1.1 (0.3)	0.25	*C4·OA*
4	C_1C_6ImNTf$_2$	octylamine	1.2 (0.3)	0.26	*C6·OA*
5	C_1C_8ImNTf$_2$	octylamine	1.2 (0.3)	0.26	*C8·OA*
6	C_1C_{10}ImNTf$_2$	octylamine	1.3 (0.4)	0.27	*C10·OA*

[a] ratio [RNH_2]/[Ru(COD)(COT)] = 0.2 used for the synthesis. [b] ratio between the total concentration of the ligand and the concentration of Ru atoms at the surface.

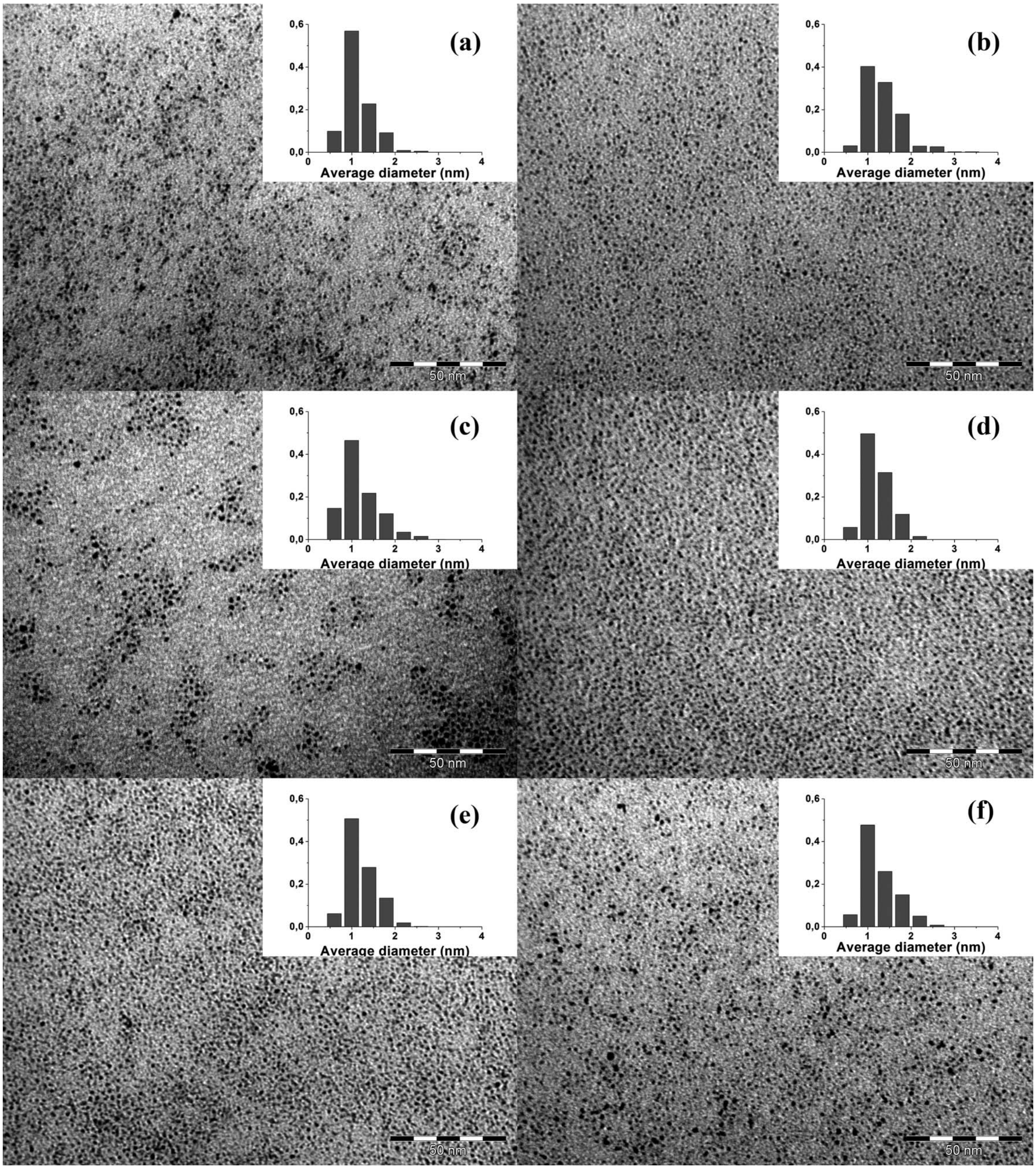

Fig. 1 a–f Left to right and up to down: colloids in ILs of *C4·OA*, *C4·HDA*, *C4·OA·NS*, *C6·OA*, *C8·OA* and *C10·OA* (see Table 1).

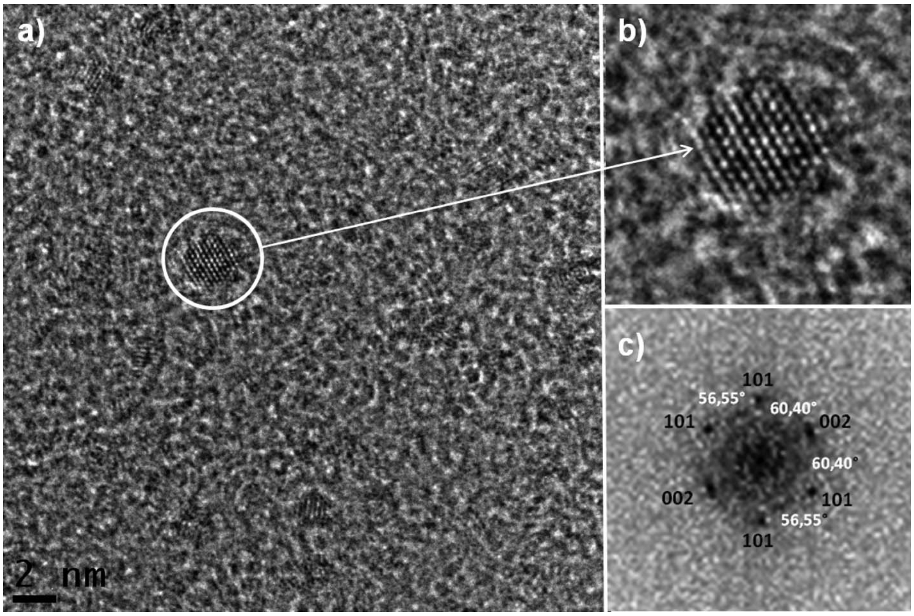

Fig. 2 a) general HRTEM image of *C4·OA*-stabilized RuNPs in $C_1C_4ImNTf_2$; b) HRTEM image of an isolated and well-crystallised *C4·OA*-stabilized Ru NP with c) FFT.

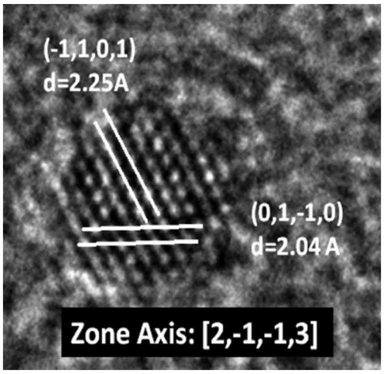

Fig. 3 High resolution image showing the fringe spacing and direction in a Ru particle. The measured distances and angles are compatible (within a 5% error) with the hexagonal structure of bulk ruthenium, showing that the particle is oriented in a [2, −1, −1, 3] zone axis.

they are spherical and do not exhibit any agglomeration. These facts indicate a better stabilization effect and a better size control when a combination of an IL and an extra ligand is used for the RuNPs synthesis.

Secondly, RuNPs synthesized in $C_1C_4ImNTf_2$ in the same reaction conditions but without any added ligand displayed a mean size of 2.3 nm,[29] whereas in the present work, RuNPs of 1.1 nm average diameter are obtained in $C_1C_4ImNTf_2$, whatever the amine, octylamine or hexadecylamine. Only RuNPs obtained in $C_1C_4ImNTf_2$ at 0 °C without stirring display a similar size. This evidences the beneficial effect afforded by the combination of an IL and a ligand to produce small and stable RuNPs.

Another important difference can be observed when considering the length of the alkyl chain attached to the imidazolium ring. As previously described,[22] there is a correlation between the size of the alkyl chain of the IL and the mean diameter of the nanoparticles. More precisely, in the absence of added ligand, the size of the nanoparticles produced in ILs follows the trend $C_1C_{10}ImNTf_2 > C_1C_8ImNTf_2 > C_1C_6ImNTf_2 > C_1C_4ImNTf_2$. This phenomenon is explained by the properties of imidazolium ILs, which show some degree of self-organization, leading to a separation between the polar (cation and anion) and non-polar domains (alkyl chains).[17–19] Since [Ru(COD)(COT)] is preferentially dissolved in non-polar regions, its local concentration is controlled by the size of the non-polar domains. This means that the number of Ru nuclei available for nanoparticle growth is dependent on the length of the alkyl chain attached to the imidazolium ring. In contrast, such a phenomenon is not observed for nanoparticles synthesized in the same ILs ($C_1C_4ImNTf_2$, $C_1C_6ImNTf_2$, $C_1C_8ImNTf_2$ and $C_1C_{10}ImNTf_2$) but in the presence of an added amine. In fact, when using octylamine, the average size of the nanoparticles is the same (between error limits) independently of the length of the alkyl chain of the IL (Table 1, entries 3–6). Furthermore, it is worth commenting that no aggregation or formation of superstructures is observed for the colloids synthesized in the presence of octylamine in $C_1C_{10}ImNTf_2$, in contrast to previous observations when no ligands were added in the reaction medium.[22]

In summary of this part, RuNPs synthesized at 30 °C in ILs in the presence of ligands do not present any agglomeration. In addition, their size is significantly smaller than that of both NPs prepared in the same ILs but in the absence of ligand, and NPs prepared in THF with the same ligand. This suggests a combined effect of both the IL and the amine on the NPs. Furthermore, no correlation was observed between the size of the alkyl chain of the IL and the size of the nanoparticles. This suggests that, while the IL is still preventing particle agglomeration, the ligand is playing the main role in controlling their size and shape. It appears therefore that the method of preparation of nanoparticles described in this paper is suitable for the controlled synthesis of small size, homogeneously dispersed and stable nanoparticles. A point of interest is that in organic solutions, the nanoparticles stabilized by amine ligands display an elongated shape and give rise to worm-shaped structures. This has not been observed in the case of Ru NPs stabilized by amines in ILs. This suggests a confinement of the amine inside the apolar domains of the ILs and perhaps an increased pressure leading to an increased association constant of the ligands in the ILs. This will be discussed in the NMR section.

2.2 Study of the role of the amine in the stabilization of the ruthenium nanoparticles

As the amine ligands appeared crucial for the size control of the RuNPs, we tried to determine their exact role by gas chromatography (GC) and NMR.

First of all, to ascertain the presence of the ligand in the colloidal solutions after their synthesis, a sample of *C4·OA* was diluted in acetonitrile and analyzed by GC. The chromatogram showed a peak corresponding to the presence of octylamine in the colloidal solutions.

The colloidal solution of *C4·OA* was further studied by NMR spectroscopy and compared to a solution of the stabilising amine in the IL. The ^{1}H NMR spectrum of an octylamine solution in $C_1C_4ImNTf_2$ shows a triplet ($J = 7$ Hz) at 2.60 ppm, corresponding to the protons attached to the Cα carbon close to the nitrogen atom of the octylamine. The other signals are not observable because of overlap with the more intense imidazolium signals. In colloidal *C4·OA*, only a broad signal from octylamine is observed at 3.15 ppm.

Fig. 4 presents ^{13}C NMR spectra registered for the free ligand in IL (Fig. 4a), for colloidal *C4·OA* (Fig. 4b), and for a mixture of the colloidal *C4·OA* with a ligand excess (Fig. 4c). In the spectrum of colloidal *C4·OA* (Fig. 4b), we can observe some differences in comparison with the spectrum of the free amine in IL (Fig. 4a). First of all, most of the signals corresponding to the free ligand (*) are missing. No signal is observed for Cα near 42 ppm as expected, but all of the other signals are very broad, including the signals corresponding to the alkyl chain near 13, 22 and 29 ppm. Similar NMR results were previously observed for RuNPs stabilized by alkylamines,[8] for which the coordination of the ligands at the particle surface led to the absence of the signal for Cα while the signals for the carbons located further away from nitrogen displayed a lower intensity and were slightly shifted. This indicates the absence of mobility for the ligand which can result either from a strong interaction between the alkyl chain and the ruthenium surface or from a confinement in the non-polar domains. When a slight excess of amine was added to the NMR tube containing the colloid, the resulting spectrum evidenced the superposition of the signals corresponding to the free amine and those corresponding to the amine coordinated to nanoparticles (t) (Fig. 4c) and therefore indicates the lack of exchange between the free ligand in the organic solvent and that which is most likely confined in the IL. This result differs from the reactions in THF for which a fast exchange between free and coordinated ligand was observed.

Table 2 Diffusion coefficients (D) of octylamine and imidazolium cations in different samples in neat ILs

Sample	D_{OA} ($m^2 s^{-1}$)	D_{Im} ($m^2 s^{-1}$)
Octylamine in $C_1C_4ImNTf_2$	5.740×10^{-11}	3.043×10^{-11}
C4·OA	3.631×10^{-11}	2.970×10^{-11}

To try and shed more light on the coordination of the amine, ^{1}H DOSY NMR experiments were performed to measure the diffusion coefficients (D) of octylamine and the imidazolium cations.

Indeed, it is described for palladium NPs in imidazolium ionic liquids in the presence of methanol, that a larger decrease in the diffusion coefficient of the cation proves that the NPs interact with the imidazolium cations and not with methanol.[31]

Two samples were thus prepared for a comparison by DOSY NMR: one containing a solution of octylamine in the neat IL (with the same concentration as the one employed for the synthesis of NPs), and the other one corresponding to the colloidal *C4·OA*. Table 2 reports the values of the diffusion coefficient (D) of the amine and the imidazolium cations in both samples.

The results show that there is almost no change in the diffusion coefficient of the imidazolium cations between the two samples, whereas the D value of octylamine is significantly lower for the colloidal *C4·OA* compared to the amine in $C_1C_4ImNTf_2$. The fact that the diffusion of the amine is decreased in the presence of the RuNPs can be explained by an interaction of the amine with the RuNP surface.

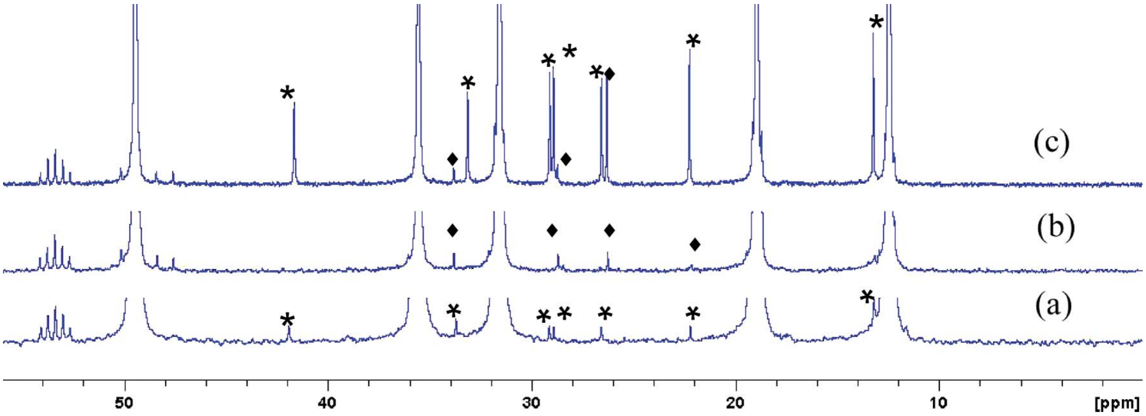

Fig. 4 ^{13}C NMR spectra of (a) octylamine in neat $C_1C_4ImNTf_2$, (b) the colloidal *C4·OA*, (c) a mixture of the colloidal *C4·OA* and octylamine (excess). Most intense peaks are from the IL. The other peaks were assigned to free (*) and coordinated amine (t). The multiplet at *ca.* 53 ppm. is CD_2Cl_2 (coaxial capillary tube). The sharp peaks (◆) were probably resulting from decomposition of the amine.

Thus, in conclusion of this part, these NMR experiments unambiguously demonstrate the coordination of the amine to the surface of the ruthenium nanoparticles. The amine ligands present at the surface of the particles are unable to exchange with excess amine as in organic solvents, probably resulting from the location of the nanoparticles inside apolar domains which isolate them from one another, preventing ligand diffusion and thus allowing them to maintain a small size and spherical shape.

2.3. Catalytic hydrogenation of toluene using ruthenium nanoparticles as the catalyst

To probe the surface state of the synthesized RuNPs, they were investigated as catalysts. In the literature, RuNPs in ionic liquids are reported as efficient catalysts for the hydrogenation of alkenes and aromatic compounds in mild reaction conditions (4 atm, 75 °C),[28] while it is known that molecular Ru compounds do not catalyse the hydrogenation of aromatic compounds.[2,32–35] We therefore studied the catalytic activity of the RuNPs synthesized in this work for the hydrogenation of toluene (PhMe) into methylcyclohexane (CyMe).

The catalytic experiments were carried out using a preformed colloidal suspension on which toluene was added, leading to biphasic toluene/IL system. More precisely, in a Schlenck tube, toluene (0.80 mmol, 0.085 ml) was added over 0.5 mL of the chosen colloid. The reaction system was stirred, kept at the desired temperature and finally filled with H_2 (1.2 bar). The H_2 pressure was kept constant for 5 h. Then the reaction was stopped, cooled down to 25 °C and quenched with acetonitrile to yield a homogeneous mixture, which was further analyzed by gas chromatography. Consequently, each point of the catalytic graph corresponds to an independent experiment.

Catalytic tests were first performed with the RuNPs synthesized in $C_1C_4ImNTf_2$ in the presence of octylamine, at different temperatures (30, 50, 75 and 100 °C), under 1.2 bar $H_2$and with a reaction time of 5 h (Table 3). The conversion obtained is low but reproducible, with a value of 4% at 30 °C, 9% at 50 °C, 17% at 75 °C and no improvement obtained at 100 °C. A temperature of 75 °C was chosen for studying the reaction with the other colloids. The results are also collected in Table 3. A slightly lower conversion is obtained with hexadecylamine instead of octylamine although the NPs have a similar size and shape, and the same amount of ligand. The observed difference can therefore be explained by the differences in the viscosity of the reaction mixtures or by a higher steric hindrance of hexadecylamine once coordinated on a RuNP surface.

We also studied the influence of the IL on the catalytic activity. For that purpose, the colloidal systems prepared in the presence of octylamine, and the $C_1C_4ImNTf_2$, $C_1C_6ImNTf_2$, $C_1C_8ImNTf_2$ and $C_1C_{10}ImNTf_2$ ILs were investigated at different reaction times (30, 60, 90, 180 and 300 min), as reported in Fig. 5. Small differences are observed when the length of the alkyl chain in the imidazolium cation increases. These variations could be due to different solubilities of toluene, methylcyclohexane and dihydrogen in the different ionic liquids, and also the differences in the viscosity of the reaction mixtures.[36,37]

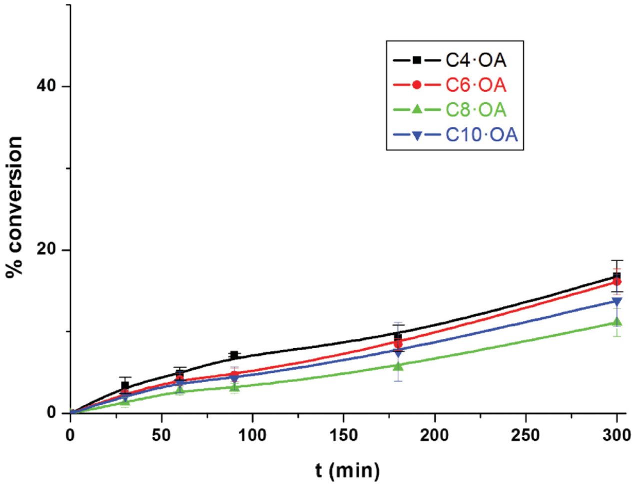

Fig. 5 Reaction profiles of the hydrogenation of toluene into methylcyclohexane, employing as catalysts colloids of RuNPs in ionic liquids with different alkyl chain lengths.

2.4. Recycling of the catalyst.

Thanks to the low vapour pressure of ILs as well as to their thermal stability, NPs dispersed in ILs are interesting systems for recycling purposes. After catalysis, the unreacted toluene (PhMe) and the hydrogenated product, methyl-cyclohexane (CyMe), can be evacuated under vacuum, allowing their separation from the colloid. Then, the relative composition of the PhMe-CyMe mixture can be determined by gas chromatography.

Table 3 Hydrogenation of toluene with the RuNPs synthesized in $C_1C_4ImNTf_2$ in the presence of amine

IL/ligand	*T* (°C)	$PhMe/Ru_T$	$PhMe/Ru_S$	Ru_S/Ru_T	% conversion	TON[a]	$k_{initial}$ (10^{-2} mol L^{-1} h^{-1})[b]
C4·OA	30	38/1	46/1	0.82	4	2	
C4·OA	50	38/1	46/1	0.82	9	4.5	
C4·OA	75	38/1	46/1	0.82	17	8	12 ± 1
C4·OA	100	38/1	46/1	0.82	17	8	
C4·HDA	75	38/1	52/1	0.73	14	6.5	
C4·OA	75	38/1	46/1	0.82	17	8	12 ± 1
C6·OA	75	38/1	49/1	0.77	16	8	8 ± 1
C8·OA	75	38/1	49/1	0.77	11	5.5	5 ± 1
C10·OA	75	38/1	52/1	0.73	14	7	7 ± 1

Reaction conditions: constant pressure of 1.2 bar of H_2; reaction time = 5 h; Ru_T = total amount of ruthenium atoms; Ru_S = amount of surface ruthenium atoms.[a] Turn over number (moles of product converted per mol of Ru_S). [b] Estimated initial rates.

We have checked the reusability of our RuNPs colloidal suspension obtained in $C_1C_4ImNTf_2$ and in the presence of octylamine. Ten consecutive experiments of toluene hydrogenation (1.2 bar H_2, 75 °C, 5h) were carried out with the same colloid (Fig. 6). After each catalytic cycle, PhMe and CyMe were vacuum-separated from the colloid. Samples of RuNPs taken after one and after ten catalytic experiments respectively were analyzed by TEM. The TEM analysis after ten catalytic cycles shows a larger mean size of the nanoparticles and a broader size distribution (1.6 ± 0.7 nm) than those observed before catalysis (1.1 ± 0.3 nm) and after one catalytic test (1.2 ± 0.6 nm). Although there is a smooth trend to lower conversions, it is worthwhile to note that after ten consecutive experiments with the same batch of nanoparticles, they remain still active.

3. Experimental

3.1. Materials and characterization methods

1-Methylimidazole (>99%) was purchased from Sigma-Aldrich and distilled prior to use. Ruthenium trichloride hydrate and anhydrous 1-chlorobutane (>99.5%) were also received from Sigma-Aldrich and used without further purification. Bis(trifluoromethanesulfonyl)imide lithium salt (>99%) was produced by Solvionic company and Zinc (A. R. Grade) by Merck and both were used as received. 1,5-cyclooctadiene (>99%) was purchased from Sigma-Aldrich and purified through a neutral alumina column. The ionic liquids were prepared according to the known method [38] dried overnight under high vacuum and stored in a glovebox. (1,5-cyclooctadiene)(1,3,5-cyclooctatriene)ruthenium, [Ru(COD)(COT)], was synthesized using the procedure reported by Pertici and Vitulli [39] Toluene was dried and purified in a MBraun SPS-800 purification system, and degassed prior to use.

Transmission electronic microscopy (TEM) experiments were performed directly in the IL media. Each solution of RuNPs in IL was analyzed *in situ* using TEM by depositing a droplet on a holey carbon film supported by a copper grid. The TEM analyses were performed at the "*Service Commun de Microscopie Electronique de l'Université Paul Sabatier*" (TEMSCAN), using a JEOL 1011 electron microscope operating at 100 kV with resolution point of 4.5 Å, and at the "*Centre Technologique des Microstructures*", UCBL1, Villeurbanne, France, using a Philips 120 CX electron microscope with acceleration voltage of 120 kV. High-resolution TEM images were obtained at the "*Service Commun de Microscopie Electronique de l'Université Paul Sabatier*" (TEMSCAN) using a JEOL JEM 2100 F at 200 kV with a resolution point of 2.3 Å. The size distributions were determined through a manual analysis of ensembles of over 300 particles found in randomly selected areas of the enlarged micrographs, with Imagetool software to obtain a statistical size distribution and a mean diameter.

Solution NMR spectra were recorded in a Bruker AV-300 spectrometer. ^1H and ^{13}C spectra were referred internally to deuterated solvents; chemical shifts are relative to Me_4Si.

2D DOSY (Diffusion Order Spectroscopy) experiments were performed on a Bruker Avance III 500 spectrometer, using the standard Bruker sequence dstebpgp3s in order to minimize convection effects when measuring short diffusion coefficients, trapezoidal gradients for shorter pulses, and the "baseopt" option for acquisition mode to get a very good baseline. The diffusion evolution time Δ was set to 100 ms and gradient pulses to 3 ms leading to $\delta = 6$ ms. The diffusion space was sampled by 32 linearly spaced gradients. Processing used the DOSY module of TOPSPIN 2.1. Temperature was set to 25 °C, and 32 dummy scans were used for temperature equilibration in the sample.

Gas chromatography analyses were performed in a HP5890 chromatograph equipped with a polymethylsiloxane column. The injector and detector temperature was set at 250 °C. For the analysis the column temperature was initially fixed at 100 °C, followed by a temperature ramp of 10 °C until reaching 150 °C.

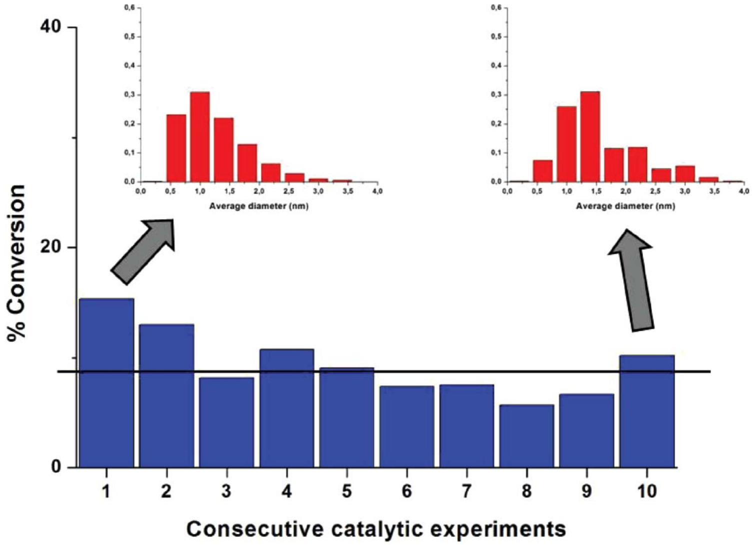

Fig. 6 Conversion of toluene into methylcyclohexane obtained for ten consecutive experiments with the same colloid *C4·OA* ($P = 1.2$ bar H_2; 75 °C; 5 h. Inside histograms show normalized size distributions of RuNPs observed after the first catalytic experiment and the tenth one, respectively. The black line represents the mean conversion (9%) calculated for all recycling experiments.

3.2. Synthesis of Ru NPs in the presence of octylamine

In a typical experiment, [Ru(COD)(COT)] (66.2 mg, 0.21 mmol) was placed in a Fischer–Porter bottle, on which the ionic liquid 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ($C_1C_4ImNTf_2$, 5 mL) and the octylamine (6.9 µL, 4.2×10^{-2} mmol) were added. The obtained mixture was a yellow suspension that was stirred for 2 h. The mixture was then frozen in a liquid nitrogen bath, and a vacuum was made. The system was fixed to 30 °C, filled with H_2 (3 bar), and stirred for 20 h. After that time, the remaining hydrogen and volatile alkanes were evacuated under vacuum. The final mixture was a black colloidal suspension that remained stable for months.

3.3. Synthesis of RuNPs in the presence of octylamine without stirring

[Ru(COD)(COT)] (66.2 mg, 0.21 mmol) was placed in a Fischer–Porter bottle, and the ionic liquid 1-butyl-3-methyl-imidazolium bis(triflruoromethanelsulfonyl)imide ($C_1C_4ImNTf_2$, 5 mL) and the octylamine (6.9 µL, 4.2×10^{-2} mmol) were added. The mixture was a yellow suspension that was stirred for 3 h. The mixture was frozen in a liquid nitrogen bath, and placed *in vacuo*. The system was thermostated to 30 °C, filled with H_2 (3 bar), and left without stirring for 3 days. After that time, the remaining hydrogen and volatile alkanes were evacuated under vacuum. The mixture was a black colloidal suspension that remained stable for months.

3.4. Synthesis of Ru NPs in the presence of hexadecylamine

In a typical experiment, [Ru(COD)(COT)] (66.2 mg, 0.21 mmol) was placed in a Fischer–Porter bottle, and the ionic liquid 1-butyl-3-methyl-imidazolium bis(triflruoromethylsulfonyl)imide ($C_1C_4ImNTf_2$, 5 mL) and the hexadecylamine (10.1 mg, 4.2×10^{-2} mmol) were added. The mixture was a yellow suspension that was thermostated to 30 °C and stirred for two hours. The system was evacuated, then was filled with H_2 (3 bar), and stirred for 20 h. After that time, the remaining hydrogen and volatile alkanes were evacuated under vacuum. The mixture was a black colloidal suspension that remained stable for months.

3.5. Catalytic experiments

In a typical experiment, 0.5 mL of one of the colloidal suspensions was placed in a Schlenk flask and toluene was added (85 µL, 0.8 mmol). The mixture was frozen in a liquid nitrogen bath, and a vacuum was made. Then, the system was thermostated to 75 °C, filled with H_2 (1.2 bar), and stirred for 5 h, keeping constant the hydrogen pressure. The reaction was quenched with acetonitrile (2 mL) and analyzed by gas chromatography.

3.6. Recycling experiments

The colloidal suspension *C4·OA* (0.5 mL) was placed in a Schlenk flask and toluene was added (85 µL, 0.8 mmol). The mixture was frozen in a liquid nitrogen bath, and a vacuum was made. The system was then thermostated to 75 °C, filled with H_2 (1.2 bar), and stirred for 5 h, keeping the hydrogen pressure constant. After that time, hydrogen was evacuated by creating a vacuum in the system, so the hydrogen was evacuated and the toluene and methylcyclohexane was collected in a trap (frozen in liquid nitrogen and connected to the Schlenk flask). The RuNP suspension is thus ready for a new catalytic experiment. Ten consecutive catalytic experiments were performed with the same batch of colloid.

The mixture of toluene/methylcyclohexane was diluted in acetonitrile and examined by gas chromatography. A copper grid of RuNPs in suspension was prepared for TEM analysis after ten consecutive experiments of catalysis. The copper grid for TEM analysis after only one catalysis experiment was prepared from an independent experiment.

4. Conclusions

Stable, small and homogeneously dispersed ruthenium nanoparticles were synthesized in imidazolium type ILs in the presence of alkylamines as ligands. Whatever the alkylchain length of the IL, the mean size of the obtained RuNPs is found to be approximately 1.2 nm. No correlation between the length of the alkyl chain of the imidazolium ring of the ILs and the size of the RuNPs was observed, in contrast to the previous results reported in ILs in the absence of ligands. ^{13}C NMR and ^{1}H DOSY NMR experiments evidence the coordination of the added amine to the NPs which explains the influence of the amine in controlling the size of the *in situ* prepared RuNPs. The obtained colloidal suspensions of RuNPs are stable for months, the ILs preventing their aggregation. Despite a moderate activity, these nanoparticles are able to catalyze the hydrogenation of toluene. Furthermore, recycling of the nanocatalyst was possible for ten consecutive times without either dramatic loss of activity or agglomeration. Thus this study demonstrates that it is possible to combine the properties of ionic liquids to confine nanoparticles in the non-polar domains ("nanoreactors") with the presence of a weak ligand which stabilizes the particles at a very small size but does not totally impede their catalytic activity.

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