

Stabilization of mono- and bimetallic nanoparticles in ionic liquids

W. Darwich¹, P. Arquillière^{1,2}, I. Helgadottir^{1,2}, P.H. Haumesser², C. C. Santini¹

¹Université de Lyon, UMR 5265 CNRS-Université de Lyon 1-ESCOPE Lyon
C2P2, ESCPE, 43 Boulevard du 11 Novembre 1918, 69616 Villeurbanne, France
²CEA, LETI, MINATEC Campus 17, rue des Martyrs 38 054 Grenoble Cedex 9, France

ABSTRACT

Unlike traditional solvents, ionic liquids (ILs) can be used to generate metallic NPs in the absence of any additive. Indeed, ILs can dissolve organometallic (OM) precursors, which readily form metallic NPs by decomposition (or reduction) under dihydrogen. This process provides suspensions of metallic NPs, with accurate size control and high stability. In this work, we investigate the mechanisms responsible for the stabilization of nanoparticles in ionic liquids. Our results indicate that mass transport limitation can contribute to the stabilization of small NPs. We also demonstrate that this approach is capable to yield NPs of most metals, provided that adequate OM precursors are found. Furthermore, upon mixing two OM precursors in the same IL, this approach is suited to form bimetallic NPs. We extend this synthesis to new systems. Hence, this approach could open a new, general and low-cost route to form mono- and bimetallic NPs, with accurate size and structure control.

Keywords: ionic liquid, nanoparticles, metal, organometallic

1 INTRODUCTION

Metallic nanoparticles (NPs) are needed in a range of applications such as the fabrication of advanced microelectronic, magnetic or optical devices [1]. However, the controlled synthesis of metallic NPs in the range of 1 to 10 nm is still an on-going challenge, as is the understanding of their stabilization and agglomeration. In particular, substantial effort has been centered on stabilizing transition-metal nanoparticles in wet synthesis processes, using polymers, ligands and organic or inorganic templates. Unlike traditional solvents, ionic liquids (ILs) can be used to generate metallic NPs in the absence of any additive [2]. Ionic liquids are molten salts at room temperature, composed of an organic cation and an inorganic or organic anion. They are thermally and electrochemically stable, non-volatile and electrically conductive. ILs can dissolve organometallic (OM) precursors, which have been shown to form metallic NPs by decomposition (or reduction) under dihydrogen [3]. This process provides suspensions of metallic NPs, with accurate size control and high stability [3-5]. However, the exact mechanisms responsible for this stabilization remain unclear.

In a first part of this work, the size dependence of RuNPs on the length of alkyl chains in the cation will be studied. Then, the unexpected size reduction of bimetallic NPs as compared to the pure metals will be described, and shown to be quite general. The synergistic effect responsible for this phenomenon will be studied in-depth for the RuCu system.

2 EXPERIMENTAL

2.1 Chemical Synthesis of Nanoparticles

The synthesis of 1-alkyl-3-methylimidazolium bistrifluoromethyl-sulphonylimide ($C_1C_n\text{ImNTf}_2$ with $n = 2$ to 18) ILs was performed from commercially available 1-methylimidazole, 1-alkylchloride (Sigma Aldrich), and lithium bistrifluoromethylsulphonylimide (Solvionic) [6]. After drying IL overnight at 10^{-8} bar, organometallic precursors were dissolved separately under inert conditions and vigorous stirring to form a solution at typically 5×10^{-2} M (Table 1). In the case of bimetallic systems, two of these solutions were mixed and stirred for 10 min in an autoclave under argon at room temperature, yielding a solution with the desired $M_1:M_2$ molar ratio.

The synthesis of the nanoparticles was conducted by decomposition of the various solutions and mixtures in a sealed reactor at temperatures between 0 and 100°C under H_2 pressure (typically 0.4-0.9 MPa) for several hours. The volatile products released during decomposition were quantified by gas chromatography in order to verify the stoichiometry of the reaction.

2.2 Characterizations

The NPs were observed by Transmission Electron Microscopy (TEM) using a Philips CM120 120 kV. For this purpose, the suspensions of NPs in IL were deposited on a TEM grid and excess IL was removed. A thin film of liquid suspension remained on the grid, which could be observed without further preparation, as ILs are virtually non-volatile and do not evaporate under high vacuum at room temperature. For each sample, a least 100 NPs were measured. Their size distribution was fitted by a lognormal law to provide mean diameter and size dispersion.

Metal	OM precursor	Tested ILs	Temperature	H ₂ pressure	Duration	NPs diameter (nm)	Refs
Ru	Ru(COD)(COT)	C ₁ C _n ImNTf ₂ n=2 to 18	0-100°C	0.4-0.9 MPa	1-4 h	1.8-6 nm upon conditions	3-5, 7, 11, this work
Cu	CuMes	C ₁ C ₄ ImNTf ₂	100°C	0.4-0.9 MPa	4 h	4-6 nm upon conditions	7, 11
Mn	MnNp ₂	C ₁ C ₄ ImNTf ₂	100°C	0.9 MPa	4 h	2.3±0.5 nm	
Ta	Np ₃ Ta=CHCMe ₃	C ₁ C ₄ ImNTf ₂	25°C-100°C	0.4 MPa	4-72 h	4-5 nm upon conditions	This work
Ni	Ni(COD) ₂	C ₁ C ₆ ImNTf ₂	100°C	0.9 MPa	4 h	5.3±0.9 nm	

Table 1: Tested precursors and conditions for the synthesis of mono-metallic NPs

3 MONOMETALLIC NANOPARTICLES

3.1 Influence of IL structure

Previous studies have shown that the decomposition of Ru(COD)(COT) under H₂ at 0°C in C₁C_nImNTf₂ yields RuNPs whose size increases from 1.1 to 2.3 nm as n increases from 4 to 8.[4] This size could be related to a specific short-length order within the ILs, whose ions form a polar backbone carrying apolar alkyl ends. For intermediate alkyl chains (n=4 to 8), these apolar ends form discrete, isolated pockets in a polar matrix. It turns out that the size of the RuNPs is comparable to and increases with the size of these apolar domains.

More recently, attempts were made to synthesize RuNPs at 100°C in C₁C₄ImNTf₂ [7]. In this case, much larger particles are formed around 4 nm with higher size dispersion. This effect can be attributed to the partial destruction of the local order within the liquid at higher temperature, along with faster diffusion of the dissolved species. In this work, this study was extended to ILs with longer chains. Indeed, in these ILs, apolar chains do not form isolated, but percolating pockets, which is not expected to favor small NPs. On the other hand, these ILs are more viscous, diffusion phenomena are much slower, leading to smaller NPs. To discover which of these effects is dominant, solutions of 5×10⁻² M Ru(COD)(COT) in C₁C_nImNTf₂ (n=2 to 18) were decomposed at 100°C under 0.9 MPa H₂ for 4 h. In all cases, RuNPs were formed, whose size was measured by TEM (Figure 1). In agreement with previous results, 4±1 nm RuNPs were found in C₁C₄ImNTf₂. Similar NPs were formed in C₁C₂ImNTf₂. For n≥6, significantly smaller RuNPs were obtained, and constant diameter of about 1.8 nm was measured for n≥8. This result indicates that for long chains, the morphology of the RuNPs is probably driven by mass transport kinetics during the decomposition reaction. This is supported by observations under environmental TEM (not shown here). The formation as well as the coalescence of RuNPs could be observed *in situ*, and were found to be slower for n>6.

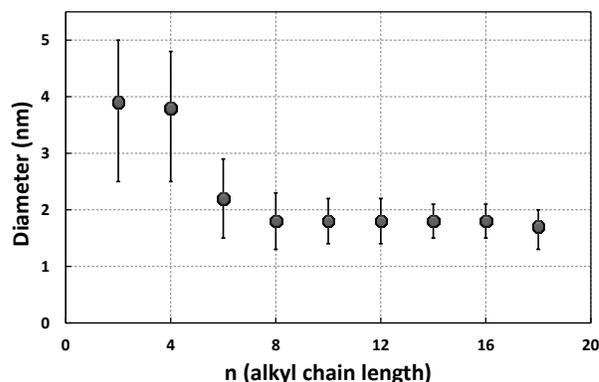


Figure 1: Size evolution of RuNPs with alkyl chain length (under 0.9 MPa H₂ at 100°C for 4 h)

3.2 Extension to other metals

NPs of various metals, listed in Table 1, have been successfully synthesized using this approach. Besides RuNPs and CuNPs described above, similar results were obtained for Ni, Mn and Ta. The latter metal is of particular interest, as TaNPs were obtained at room temperature. To our knowledge, other techniques require much higher temperatures (typically 800°C) to form TaNPs [8,9].

This demonstrates that our approach is quite general, capable to yield NPs of most metals in ILs, provided that adequate OM precursors are found. Suitable compounds only need to:

- Be soluble in the desired IL
- Decompose under H₂

4 BIMETALLIC NANOPARTICLES

This synthetic strategy can be further generalized by mixing and decomposing two OM precursors to form bimetallic NPs.

4.1 Ru and Cu

This approach was first tested on Ru and Cu. Surprisingly, upon mixing Ru(COD)(COT) and CuMes, significantly smaller NPs were obtained, with narrower size distribution, as compared to pure Ru and pure Cu [7]. As shown in Figure 2, this holds true on a very wide composition range ($\chi_{Cu} = 0.005$ to 0.91, where χ_{Cu} is the molar ratio of Cu in the mixture). Such a size reduction indicates some interaction between the two metals, which is quite surprising, considering that Cu and Ru are not miscible and do not form alloys [10]. Therefore, several experiments were conducted to elucidate the structure and mechanism of formation of these metallic NPs [11]. The following observations were made:

- The decomposition of Ru(COD)(COT) is much faster (several minutes) than the reduction of CuMes (several hours),
- The reaction of CuMes onto pre-formed RuNPs leads to larger NPs, where Cu lies around Ru (as seen by EELS),
- On RuNPs formed by decomposition under D_2 , the reaction of CuMes under argon releases deuterated mesitylene,
- The evaporation of Cu atoms into a suspension of RuNPs forms separate CuNPs, leaving the RuNPs untouched.

From these observations, it can be concluded that the interaction between the two metals results from the decomposition of CuMes by the rapidly formed RuNPs. More precisely, CuMes reacts with surface hydrides present at the surface of Ru clusters, $[Ru]_s-H$ [4]. This reaction blocks further growth of RuNPs, stabilizing smaller NPs, even with a small amount of Cu. Another consequence is that the resulting bimetallic NPs do probably have a core-shell structure, with Ru in the core and Cu in the shell.

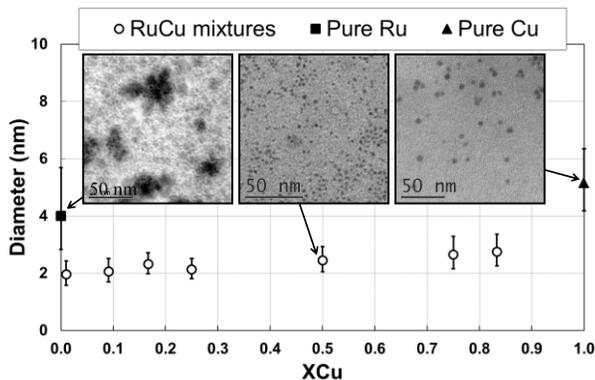


Figure 2: Size evolution of RuCuNPs with Cu content (in $C_1C_4ImNTf_2$, under 0.9 MPa H_2 at 100°C for 4 h)

4.2 Other systems

In this work, the exploration of bimetallic systems was extended to RuNi, NiCu and RuTa (Figures 3-5). RuTa and

RuNi behave like RuCu: smaller NPs with reduced size dispersion are formed. For NiCu, the size is not significantly reduced, but the mixtures yield narrower size distributions, indicating some interaction between the two metals.

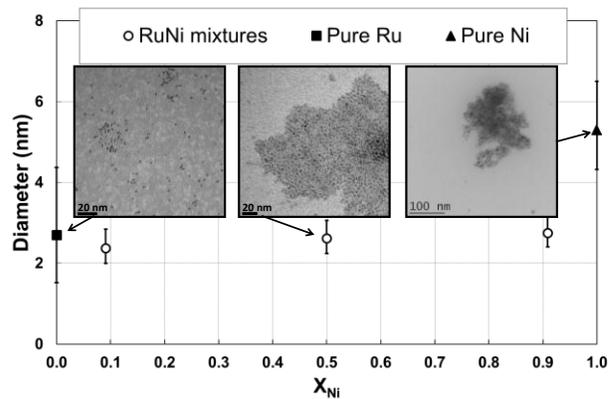


Figure 3: Size evolution of RuNiNPs with Ni content (in $C_1C_6ImNTf_2$, under 0.9 MPa H_2 at 100°C for 4 h)

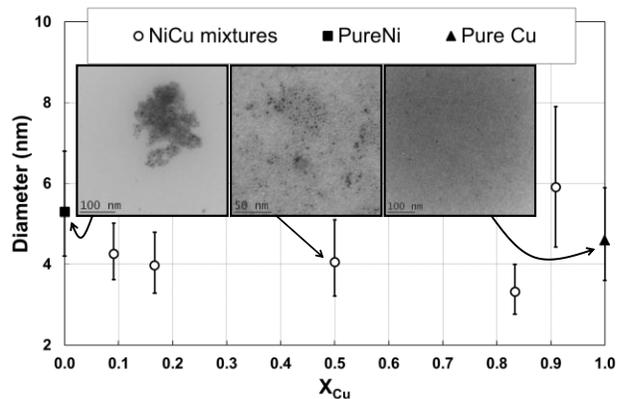


Figure 4: Size evolution of NiCuNPs with Cu content (in $C_1C_6ImNTf_2$, under 0.9 MPa H_2 at 100°C for 4 h)

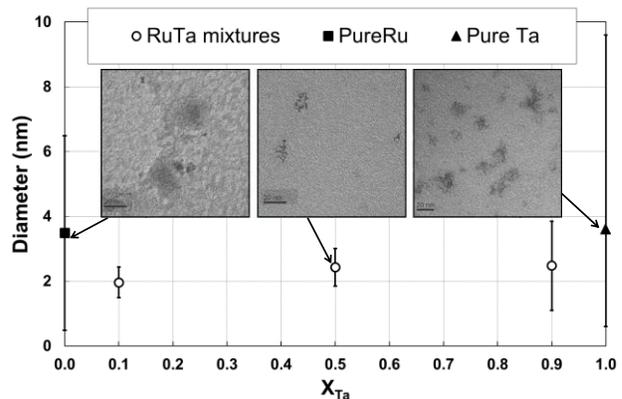


Figure 5: Size evolution of RuTaNPs with Ta content (in $C_1C_4ImNTf_2$, under 0.4 MPa H_2 at 100°C for 4 h)

In the case of RuTa, this synthesis was also run in two separate steps, starting with pre-formed, well-dispersed Ru NPs in IL. After addition of Ta-Schrock (1:1 molar ratio) and thermal treatment at 100 °C for 4 h under Ar (and not H₂), NPs were still observed, without precipitation of Ta. Their size histogram is shifted to slightly larger sizes than for the initial RuNPs (Figure 6). Moreover, the formation of neopentane was assessed by GC-MS analysis of the gas phase. This confirms that the Ta OM precursor reacted with the [Ru]s-H, similarly to the CuMes. Further characterization of the bimetallic NPs is under progress, to reveal their internal structure (nanoalloy or core-shell ?).

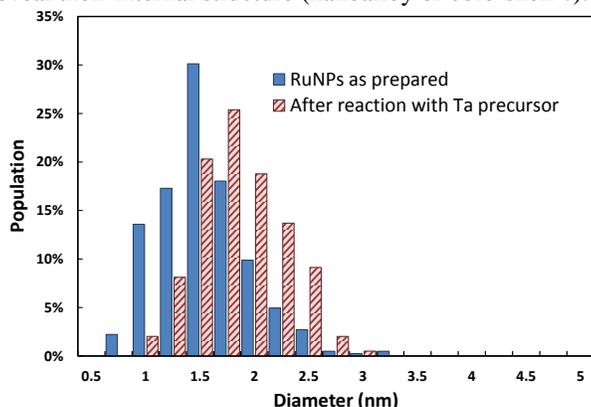


Figure 6: Size distribution of RuNPs before and after reaction with Ta precursor under Ar at 100°C for 4 h

5 CONCLUSIONS

In this work, we investigate the mechanisms responsible for the stabilization of nanoparticles in ionic liquids. For that purpose, experiments were performed in ILs with different structures (isolated or percolating apolar domains). In the case of long chains, where NPs are a priori not supposed to be stabilized by a templating effect from the IL, small NPs are nevertheless obtained, indicating that mass transport becomes limiting in these more viscous liquids. Interestingly enough, we also demonstrate the general character of the synthesis of metallic nanoparticles in ionic liquids. This approach is shown to be capable to yield NPs of most metals, provided that adequate OM precursors are found, which are soluble in the desired IL and decompose under H₂.

Furthermore, the synthesis of bimetallic NPs is also extended to new systems. Upon mixing two OM precursors in the same IL, NPs with reduced size distribution (and in most cases reduced size as well) are obtained for RuNi, NiCu and RuTa. This indicates that during decomposition, the two metals interact to probably form bimetallic NPs. Again, such a behavior could be quite general.

Hence, this approach could open a new, general and low-cost route to form mono- and bimetallic NPs, with accurate size and structure control.

ACKNOWLEDGEMENT

The authors wish to thank Pr. Suzanne Giorgio for environmental TEM observations. This work was partially funded by the french Région Rhône-Alpes through the ARC6 program.

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