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Influence of the self-organization of ionic liquids on the size of ruthenium nanoparticles : Effect of the temperature and stirring.

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The size of ruthenium nanoparticles is governed by the degree of self-organization of imidazolium based ionic liquid in which they are generated from (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium : the most structured the ionic liquid, the smallest the size.

Introduction

The use of metal nanoparticles (MNPs) is a new and very promising field for catalysis as their small sizes lead to high surface/volume ratios and may result in continuous variation of surface metallic atoms possibly located in different crystallographic positions (corners, edges, faces). Controlling the size of MNPs and consequently the resulting number of "active sites" is still a challenge whatever solvent used (organic, aqueous).[1-4] Some particular media such as polymers (e.g. polyvinylpyrrolidone), dendrimeric materials or mesoporous oxides offer the opportunity, by isolating the nuclei, to control the size and distribution of the MNPs.[5,6]

Recently, it has been highlighted that ammonium and particularly imidazolium based ionic liquids (ILs) stabilize MNPs probably by acting as a protective shell (electrostatic stabilization) or as a "surface ligand" (steric stabilization by coordination of anion, η^5-coordination of imidazolium cation, N-heterocyclic carbene, …).[7] Moreover, imidazolium based ILs possess a high degree of self-organization due to hydrogen bond network between cations and anions.[8-10] Besides they are also constituted of polar or nonpolar microdomains.[11]

Consequently ILs present two interesting effects for synthesis of MNPs.[12] On one hand, they can act as a stabilizer (as ionic ligand or neutral ligand of MNPs) and on other hand, they are able to isolate MNPs, due to their structuration in microdomain and prevent aggregation. Even if the first aspect has been well documented, to our knowledge, no direct correlation between the self-organization of ILs and the resulting size of the MNPs generated *in situ* have been reported in the literature. Our approach in this work is to establish if their 3D organization could affect the size of the MNPs generated *in situ*.

Results and discussion

In organic solvent, the decomposition in mild conditions of (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium (0) complex, Ru(COD)(COT), under a dihydrogen atmosphere gives ruthenium nanoparticles (RuNPs), by releasing cyclooctane (COA).[13]

$$Ru(COD)(COT) + H_2 \rightarrow RuNPs + COA$$

The synthesis of RuNPs in imidazolium based ILs (1-butyl-3-methylimidazolium hexafluorophosphate, tetrafluoroborate and trifluoromethanesulfonate) under 4 bar of hydrogen at 75°C for 18h affords RuNPs with a mean size of 2-2.5nm.[14]

In this work, Ru(COD)(COT), totally dissolved in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($BMIMNTf_2$), which is liquid until -6°C, has been decomposed under dihydrogen at 0 °C and 25 °C, and in the presence or absence of stirring.

In a glove box, $BMIMNTf_2$ (10mL) is introduced in a 500mL glass autoclave, then Ru(COD)(COT) (135mg, 0,43mmol, C=0.043mol/L) is dissolved at room temperature under vigorous stirring during 1h resulting in an homogenous yellow solution. The autoclave is located in a regulated temperature bath (25°C or 0°C). In all experiments, no precipitation of Ru(COD)(COT) was observed. After evacuation of argon atmosphere under vacuum, the autoclave was pressurized with 4bar of dihydrogen, during 18h for reactions performed at 25°C and at 0°C under stirring, and 3 days at 0°C without stirring.††† After evacuation of COA under vacuum, a black colloidal suspension of RuNPs is obtained which is stable for several months under argon atmosphere at room temperature. In contrast to previously described RuNPs synthesis,[14] the separation of nanoparticles from ILs was not possible by either centrifugation or addition of several types of solvents. Consequently, TEM experiments were performed directly in the ILs media.

- At 25°C under stirring, the RuNPs are homogeneously dispersed with a mean size of 2.4 +/- 0.3 nm.
- At 0°C under stirring, the RuNPs have a mean diamater of 0.9 +/- 0.4 nm. These particles are agglomerated in a kind of big cluster of 2-3 nm.
- At 0°C without stirring, the RuNPs have a mean diameter of 1.1+/-0.2nm. Interestingly and in contrast to the previous case,

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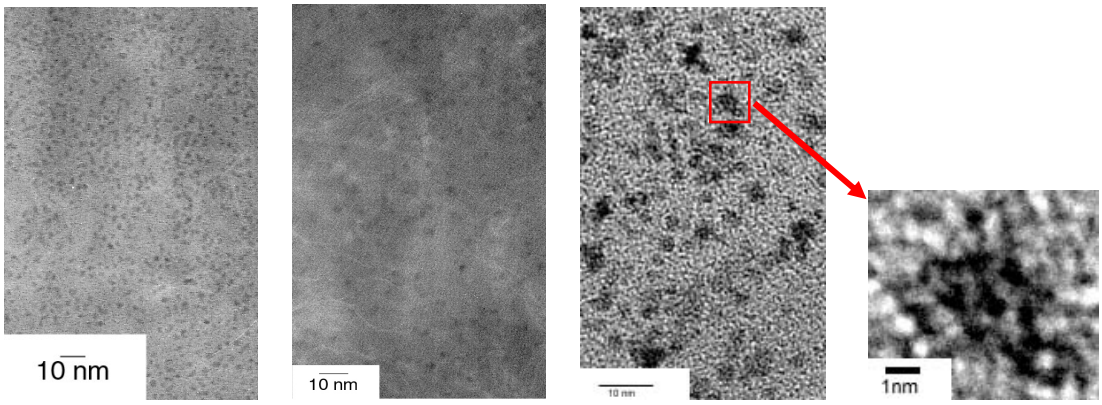

Fig. 1. *In situ* TEM micrographs of RuNPs in $BMIMNTf_2$ prepared at room temperature under stirring (left), without stirring at 0°C (middle) and under stirring at 0°C (left and zoom).

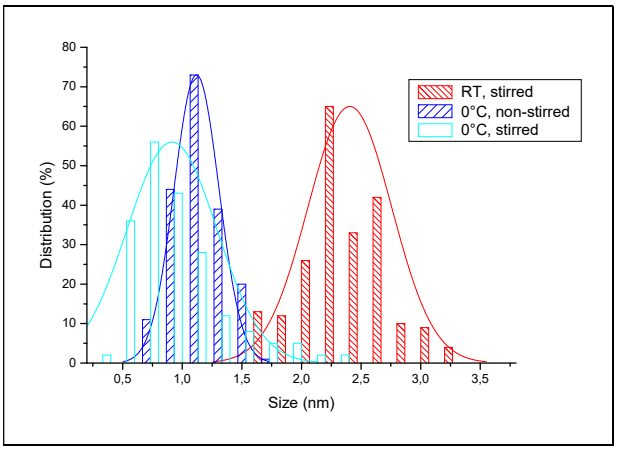

Fig.2 Size histrograms of RuNPs synthesized in $BMIMNTf_2$ in various conditions.

display an extremely narrow size distribution and are not agglomerated (Figure 1 and 2).

By comparison of our results with those of litterature, we observe that the size of RuNPs synthesized in ILs at 25°C and at 75°C are similar. Theses results confirm that ILs limit the crystal growth of RuNPs due to stabilizing factors (electrostatic or steric stabilization) as already proposed.[7]

When we consider now results obtained at 0°C, the RuNPs are smaller (c.a. 1nm) than at 25 or 75°C.

The effect of the temperature on the size of RuNPs is the inverse in ILs to that observed in THF/MeOH mixture : low temperatures favor high particle size and reversibly high temperature favor small particles size. In this latter media, it suggested[13] that the COA pockets generated *in situ* during the decomposition of Ru(COD)(COT) have a size which decreases when temperature increases. The segregation of Ru° nuclei occurs exclusively inside these pockets. Therefore the higher the temperature, the smaller the size of the particles. [4] To sum up, in THF/MeOH, the presence of small and well separated pockets leads to small and homogenous RuNPs.

In contrast to THF/methanol, the size of the RuNPs in ILs decreases with the temperature. This effect suggests that the nanoparticle precursors and/or Ru nuclei in $BMIMNTf_2$ are better isolated at 0°C than at 25°C : the organization of ILs should be better maintained at low temperatures, the confinement of nuclei in nonpolar microdomains should be more efficient and afford smaller particles.

However, as it often observed in nanoparticle synthesis, the presence of stirring at 0°C perturbs this 3D organization and leads to partial agglomeration of the small size nanoparticles[15] into larger aggregates. Therefore the fact that ILs are structured fluids with segregated polar and nonpolar domains seems to be the major cause preventing the nuclei from coalescing.

Conclusion

The well-known presence of microphase segregation between polar and nonpolar domains in ILs is a novel way of understanding their solvent properties and their ability to interact with different species. In particular, ILs could act as supramolecular matrices, whose size will be dictated by the design of the cation/anion combinations.

In summary these experiments i) show that nanoparticle synthesis in mild conditions may be used to reveal the fine structures of complex media such as ionic liquids and ii) allow the formation of very well-defined nanoparticles of very small size, a size generally difficult to control in other media.

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Notes and references

† 1-methylimidazole (>99%), 1,2-dimethylimidazole (>98%) were purchased from Aldrich and were distilled prior to use. Ruthenium trichloride hydrate and anhydrous 1-Chlorobutane (>99.5%) were received from Aldrich and used without further purification. Bis(trifluoromethanesuflonyl)imide lithium salt (>99%) was produced by Solvionic company and Zinc (A. R. Grade) by Merck and they are used as received. 1,5-Cyclooctadiene (>99%) was purchased from Aldrich and purified through neutral alunima column. Ionic liquid were prepared according to the known method, 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 *et al.*[16]

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†† Ruthenium nanoparticles were formed in $BMIMNTf_2$ by decomposition of Ru(COD)(COT) under hydrogen. In a typical experiment, 133mg of Ru(COD)(COT) is dissolved in 10mL of IL. The solution was treated with 4 bar hydrogen under vigourous stirring at room temperature. After few minutes, a black solution was formed. A drop of colloidal suspension was deposited directly on carbon film coated TEM grid forming a thin film of colloidon. TEM analysis was carried out in Transmission Electron Microscope Philips CM200 operated with 200 kV acceleration voltage with point resolution at 1.9Å or in JEM 2010 operated at 200 kV with point resolution 2.3Å.

††† Note that whatever the experimental conditions, the diffusion of dihydrogen in ILs takes place. Attempt to form RuNPs from Ru(COD)(COT) in $BMIMNTf_2$ without dihydrogen failed even under heating up to 150 °C.

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