“Ligand-Free” Metal-Nanoparticles in Ionic Liquids.

R. Marcos Esteban, F.M. Alberti, D. Marquardt, H. Meyer, C. Rutz, K. Schütte, C. Vollmer, C. Janiak*

Heinrich-Heine Universität Düsseldorf, Institut für Anorganische und Struktur Chemie,
Universitätstraße 1, 40225 Düsseldorf, Germany

Raquel.Marcos.Esteban@uni-duesseldorf.de

Metal-nanoparticles (M-NPs) are of significance due to their versatile applications in many different areas of medicine, science or industry [1] especially in catalysis due to their high surface area and activity [2] as well as excellent scaffolds for the fabrication of novel chemical and biological sensors. [3].

In this context, we have been interested during the last few years in the synthesis and stabilization of metal nanoparticles (M-NPs) in ionic liquids (ILs) [4]. Ionic liquids are defined as molten salts with melting points below 100°C. Their tunable physicochemical properties by selecting an appropriate combination of cation and anion together with their low vapor pressure offer many advantages over common solvents [2, 4] In the process of the generation and stabilization of M-NPs, ILs generate a protective layer which avoids the use of external stabilizing agent like coordinating ligands, encapsulating polymers or micelles (Fig.1) and prevents M-NPs from aggregation and agglomeration processes.

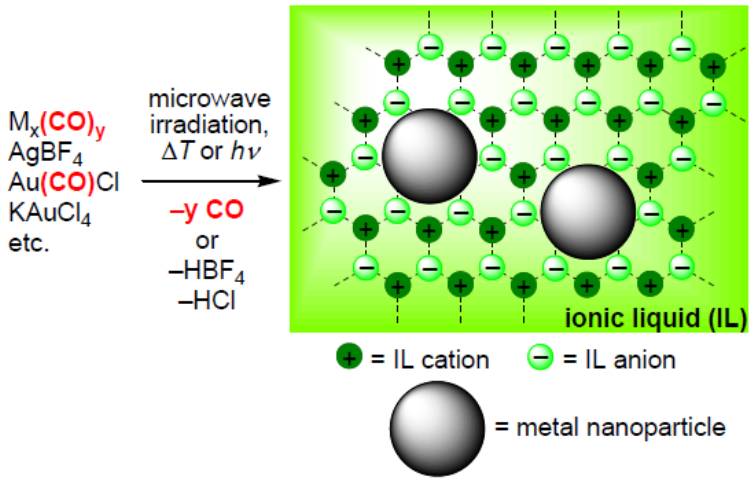

Fig.1. Ionic Liquids as a template for the Metal-nanoparticles synthesis without external stabilizations.

M-NPs can be easily synthesized in ionic liquid from different metal salts (for example MX_n where M = Au, Cu X = Cl, BF_4^-, NO_3^-, $KAuCl_4$) or metal carbonyl precursors ([Au(CO)Cl] or $M_x(CO)_y$ where M = Pd, Mn, Rh, Ru, Ir, W) by reduction photo-induced or microwave assisted, hydrogen atmosphere or thermal decomposition [5].

In terms of catalysis, the stabilization in IL of M-NPs from metal carbonyl compounds is very interesting as they avoid the presence of undesired co-ligands (CO is easily removed) which may interfere in the catalytic activity of the M-NPs.

We have recently described the successfully catalytic hydrogenation of cyclohexene and benzene Rh- , Ir- or Ru-NPs in ILs (Fig.2.) [6], as well as the deposition of Ru- and Rh-NPs on graphene sheets in IL for the same catalytic reactions [7].

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[3] See, for example: K. Saha, S. S. Agasti, C. Kim, X. Li, V. M. Rotello, *Chem. Rev.* **2012**, *112*, 2739-2779.

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