Organic phase stabilization of rhodium nanoparticle catalyst by direct phase transfer from aqueous solution to room temperature ionic liquid based on surfactant counter anion exchange†

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We describe the organic phase transfer of surfactant-stabilized rhodium nanoparticles previously synthesized in an aqueous solution of N,N-dimethyl-N-dodecyl-N-(2-hydroxyethyl)ammonium chloride (HEA12Cl); the addition of $LiN(Tf)_2$ to the aqueous suspension of Rh–HEA12Cl transferred the hydrosol nanoparticles to an ionic liquid phase.

Noble metal nanoparticles have been extensively investigated during recent years due to the various application areas of those nanomaterials.[1] As catalysts,[2] these systems show great potential but their use is limited to the solvent in which the nanoparticles were prepared. In most cases, the choice of solvent (water, organic) depends on the nature of the precursor: salts or organometallic compounds. In this context, several groups have developed interesting approaches to permit the phase transfer of the nanoparticles. The phase transfer from an aqueous phase to an organic phase is carried out by strong coordinated ligands (thiols and amines)[3–6] or traditional phase transfer reagents such as TTAB or TOAB.[7,8] The increased interest in room-temperature ionic liquids (RTILs) shown by chemists is due to their high performance in catalytic reactions and their potential as a 'green' recyclable alternative to the traditional organic biphasic system.[9] So, these compounds have been used as media for clean liquid–liquid extraction processes due to their immiscibility with water and several organic solvents.[10]

Recently, metal nanoparticles have been synthesized in room temperature ionic liquid and used as catalysts for alkene or arene hydrogenations.[11] The classical route for active nanoparticle preparation is the hydrogen pressure reduction of organometallic precursor dissolved in an ionic liquid phase. Here we describe an original approach for the one-step transfer of Rh(0) nanoparticles protected by the non classical room temperature ionic liquid N,N-dimethyl-N-dodecyl-N-(2-hydroxyethyl)ammonium trifluoro-methanesulfonimide salt ($HEA12N(Tf)_2$) starting from surfactant-stabilized Rh(0) hydrosol nanoparticles. We report the complete transfer of noble metal nanoparticle catalyst by anion exchange from water to ionic liquid in aerobic conditions (Fig. 1).

The aqueous suspension of Rh–HEA12Cl was prepared under ambient air. As similarly reported,[12,13] an aqueous solution (5 ml) of the precursor $RhCl_3 \cdot 3H_2O$ (10 mg, 3.8×10^{-5} mol) was quickly added to an aqueous solution of the surfactant N,N-dimethyl-N-dodecyl-N-(2-hydroxyethyl)ammonium chloride
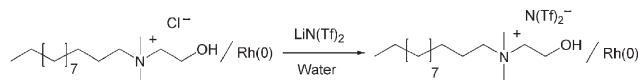

Fig. 1 Organic phase transfer of Rh(0) hydrosol nanoparticles from water to room temperature liquid ammonium salt $HEA12N(Tf)_2$.

salt (HEA12Cl) (5 ml, 1.85×10^{-3} mol) containing sodium borohydride (3.6 mg, 9.5×10^{-5} mol) under vigorous stirring.

The reduction occurs instantaneously and the Rh(0) colloidal suspension is characterized by a color change from red to black. Fig. 2a shows the TEM of the aqueous suspension of Rh(0)/HEA12Cl. The average diameter of the nanoparticles was 2.4 nm, measured with an automatic counting objects program based on shape recognition. Then, a solution of $LiN(Tf)_2$ (1.85×10^{-3} mol) was slowly added under vigorous stirring to the Rh(0) aqueous suspension. After five minutes, the $Rh(0)/HEA12N(Tf)_2$ ionic liquid phase appears. During the counter anion exchange, the hydrophilic part of the surfactant is tuned to a hydrophobic group and the nanoparticles are embedded into a protective shape of $HEA12N(Tf)_2$.

The aqueous phase turned from black to colorless, which indicated a complete phase transfer of Rh nanoparticles (Fig. 3b). The reaction is followed by UV-Vis spectroscopy.

Before addition of $Li(NTf)_2$, the UV-Vis absorption spectrum showed an absorption band at 250 nm. After addition of $Li(NTf)_2$, the absorption disappeared completely, indicating a total transfer of Rh nanoparticles. TEM observations of the resulting ionic liquid phase show that the average particle size of the system Rh–$HEA12N(Tf)_2$ was 2.8 nm (Fig. 2b). During the transfer, no visual signs of aggregation were observed, confirming an efficient phase transfer route by the anion exchange from Cl^- to $N(Tf)_2^-$. ICP-MS‡ analysis shows that the amount of chloride anion, which contributes to the stabilization of Rh(0) colloids in the aqueous phase, represents less than 4 ppm in the ionic liquid phase containing nanoparticles. This result indicates that the stabilization occurs only by interaction combination (charge and steric effects) induced by $HEA12N(Tf)_2$ at the surface of the Rh nanoparticles without any chloride effect. The counter anion exchange with PF_6^- leads to a black precipitate of Rh–$HEA12PF_6$ due to the non room temperature liquid property of $HEA12PF_6$. Thus, this solid system cannot be used in biphasic liquid–liquid hydrogenation.

After several washings with clean water the ionic liquid phase was dried under reduced pressure at 60 °C to remove water traces and diluted into 3 ml of the traditional 1-n-butyl-3-methylimida-zolium hexafluorophosphate ($BMI(PF_6)$) ionic liquid to facilitate the use of the system in a catalytic reaction.
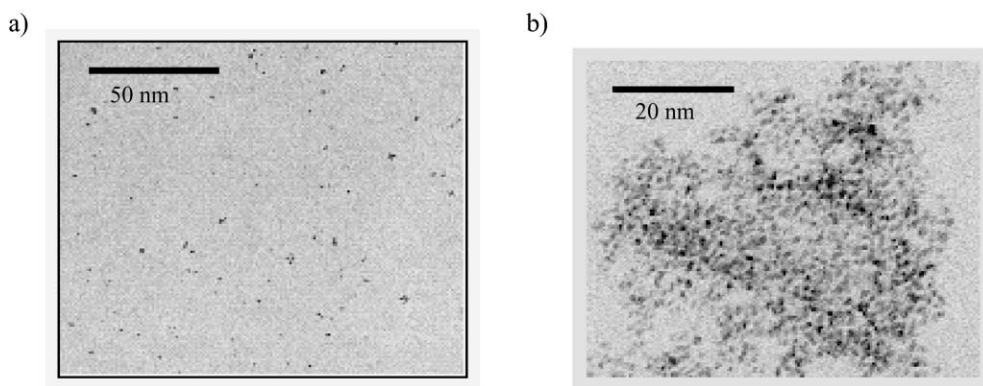

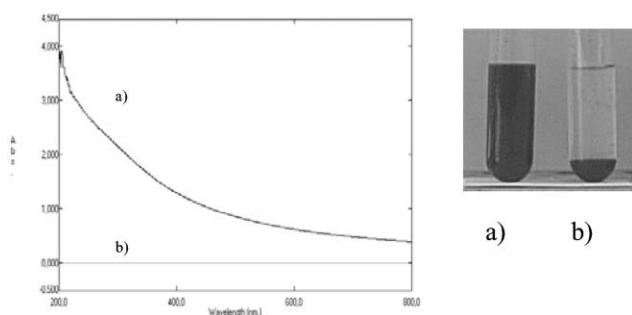**Fig. 2** TEM images of Rh–HEA12Cl (a) and Rh–HEA12N(Tf)$_2$ (b).

Fig. 3 UV-Vis absorption spectrum of Rh nanoparticles in aqueous solution of HEA12Cl (a) before addition of LiN(Tf)$_2$, (b) after addition of LiN(Tf)$_2$.

Preliminary trials of the Rh–HEA12N(Tf)$_2$ in (BMI)PF$_6$ were performed in the hydrogenation of styrene in biphasic media. The hydrogenation was performed at 25 °C and at atmospheric hydrogen pressure. The exocyclic double bond of styrene was completely reduced to ethylbenzene after one hour with a TurnOver Frequency (TOF) = 100 h^{-1} based on the amount of rhodium introduced. After the first run, no visual agglomeration was observed and the Rh(0) suspension could be reused without loss of activity for a second run after diethyl ether extraction (TOF = 98 h^{-1}).

No aromatic ring hydrogenation was observed at atmospheric hydrogen pressure and room temperature but promising catalytic hydrogenation performances on various substrates by this original system under hydrogen pressure are being actively investigated.

In contrast with gold nanoparticles transferred by strong ligands or ammonium salts described by Chujo and co-workers[3] and Wei and co-workers[7] respectively, neither coordination between ionic liquid and metal nanoparticles nor supplementary reagents were used. We have demonstrated an efficient route for phase transfer of Rh(0) nanoparticle catalysts from aqueous to ionic liquid media. Nanoparticles can be easily prepared in RTIL by anion exchange of the surfactant HEA12Cl with LiN(Tf)$_2$. The phase transfer occurred instantaneously and the resulting nanoparticles in ionic liquid have shown an efficient activity for the *exo*-double bond hydrogenation of styrene in biphasic media.

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