



Heterogeneous catalyst preparation in ionic liquids: Titania supported gold nanoparticles



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ABSTRACT

This work reports the use of ionic liquids (ILs) as solvent for the synthesis of Au/TiO₂ heterogeneous catalysts. It is shown that the versatility of the physico-chemical properties of ILs makes them interesting solvents for a broad control of supported metal nanoparticles (NPs) size and for a fine-tuning of metal–support interaction. Synthesis and deposition of Au NPs on TiO₂ are carried out through a colloidal route in imidazolium-based ILs (1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) and trifluoromethanesulfonate (BMIMOTf)) and in a Deep Eutectic Solvent (DES, choline chloride and urea). The stabilization of the dispersed NPs and their deposition on an oxide carrier is investigated in pure ILs and in the presence of extra stabilizing agents (1-methylimidazole or polyvinylpyrrolidone). In the absence of TiO₂, the NPs stability varies with the composition of the IL (BMIMOTf > BMIMPF₆ > DES) and is critically depending on the addition of an extra stabilizing agent (SA). Conversely, when gold NPs are synthesized in the presence of TiO₂ in imidazolium ILs, the addition of a SA is no longer required since the oxide support acts as a stabilizer for the gold colloids and prevents aggregation of NPs. A detailed XPS investigation of the surface composition of the TiO₂-supported gold catalysts shows that the cationic part of the imidazolium ILs on the one hand and urea in DES on the other hand are co-adsorbed with gold NPs upon deposition on TiO₂, probably decorating and stabilizing the Au NPs. The fate of the anionic part of the ILs (PF₆⁻, OTf⁻ and Cl⁻) is highly depending on the type of IL. Limited surface adsorption is reported for triflate (BMIMOTf) and chloride anions (DES), the latter being fully removed upon calcination, while PF₆⁻ (BMIMPF₆) remains adsorbed on the surface during Au NPs deposition and leads to PO_x^{δ-} and F⁻ surface species upon calcination. The surface composition controls the intrinsic catalytic activity (TOF) in the selective hydrogenation of butadiene. It is shown that the surface doping of supported Au NPs with P and F anionic deposits (synthesized in BMIMPF₆) has a promoting effect for the intrinsic catalytic activity.

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1. Introduction

Ionic liquids (ILs) are a new class of promising solvents with unique properties such as high thermal and chemical stability, very low vapor pressure and a good ability to dissolve a wide variety of organic and inorganic compounds [1,2]. These characteristics make them attractive for practical applications in various fields of research such as energy storage for example since ionic liquids are interesting candidates for substituting conventional electrolytes in

electrochemical energy devices [3]. In the field of catalysis, ionic liquids are intensively studied for homogeneous reactions in biphasic processes [4–7] or for supported ionic liquid phase systems (SILP) in order to immobilize molecular homogeneous catalyst on a support [8]. Conversely, the use of ionic liquids as solvent for synthesizing heterogeneous catalyst is seldom reported [9–11]. However, the versatility of their physico-chemical properties makes them interesting solvents for a wide control and modulation of the speciation and solubility of metal precursors and for a fine-tuning of metal–support interactions as compared to water, a solvent with exceptional but limited properties.

Ionic liquids are most commonly composed of an organic cation such as dialkylimidazolium, alkylammonium, alkylpyridinium and of an inorganic anion such as tetrafluoroborate, hexafluorophosphate or halide. ILs are characterized by a high degree of self

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organization at the molecular scale with hydrogen bond networks and continuous tridimensional networks of ionic channels coexisting with non-polar domains [12,13]. The segregation of polar and non-polar domains in imidazolium-based ILs has a large influence on their solvation properties and their ability to interact with different species [14]. Polar substrates are preferentially dissolved in polar domains and non-polar compounds in non-polar ones [15–20].

Imidazolium-based ILs have been largely studied in the literature, but suffer from some drawbacks such as potential toxicity, poor biodegradability and high cost. Hence, a new class of greener solvents has started to emerge with the introduction of deep eutectic solvents (DES), which are liquids at temperatures lower than 100 °C, and are synthesized by mixing two inexpensive and safe components self assembled through hydrogen bonding to form eutectic mixtures [21]. DES are generally composed of a quaternary ammonium salt (e.g. choline chloride) and a hydrogen bond-donor (e.g. urea) and cannot really be considered as ILs, per se, because both components are not ionic [21]. However, such distinction is not made in this work and the term ILs designates both imidazolium-based and DES solvents.

ILs are also increasingly used as solvents for the preparation of metal nanoparticles (NPs) through the reduction of a metallic precursor by molecular hydrogen [5,6,22,23] or strong reducing agents such as NaBH_4 and LiBH_4 . However, the role of the ILs on the NP stabilization is still poorly understood. It was previously reported that for imidazolium ILs the nature of the anion, including its electronic and steric properties, is one of the key factors determining the size and shape of small nanostructures [24]. However, the respective roles of the cationic and anionic parts of ILs on the stabilization and decoration of metal NPs is still a matter of debate with contradictory results reported in the literature [25]. Some reports claim that NPs are stabilized through the cationic component of the IL via parallel adsorption of the imidazolium cation [26] or through interactions with a deprotonated imidazolium cation (N-heterocyclic carbene), at least transiently [27–32]. Other reports showed that the stabilization is controlled by the anion of the IL in interaction with the metal surface through F (for BMIMPF_6 and BMIMBF_4) or O (for $\text{BMIMCF}_3\text{SO}_3$) atoms [23,33]. As a matter of fact, Raman studies of Ag NPs synthesized in BMIMBF_4 revealed direct interaction of the anion with the surface of the metallic NPs [34]. Finally, a combined cationic and anionic stabilization was also proposed [25,35] where interaction of the IL with the metal NPs occurs through the existence

of mixed cationic–anionic aggregates of the type $([(\text{Imidazolium cation})_x(\text{anion})_{x-n}]^n)^+[(\text{Imidazolium cation})_{x-n}(\text{anion})_x]^{n-})_n$ [32].

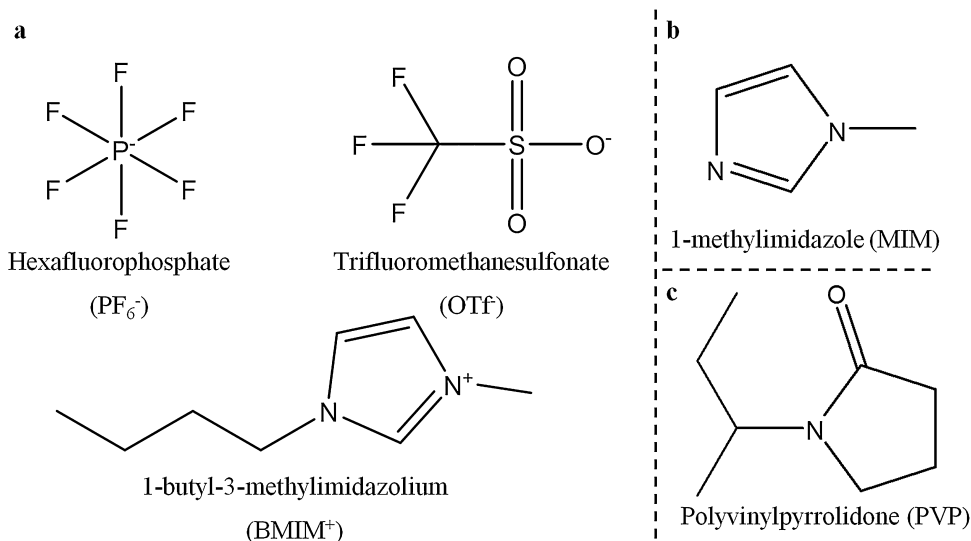
The deposition of metal NPs on high surface-area oxide supports for the preparation of oxide-supported heterogeneous catalysts in ionic liquids adds a level of complexity to the issues raised above since the growth and stability of as-synthesized NPs will now be controlled by a three-partner interaction involving the surface of the oxide support, the NPs and the components (anionic and cationic part) of the IL. This issue has been seldom addressed since very few studies are reported in the literature on the deposition of ILs-stabilized NPs on oxide carriers and its influence on the catalytic activity [9–11].

Hence, the present work aims at investigating the influence of the type of IL (imidazolium-based and DES) on the growth and deposition mechanism of Au NPs on TiO_2 . The catalysts obtained are evaluated in the selective hydrogenation of butadiene into butenes in the presence of an excess of propene, a model reaction for the purification of olefin streams largely developed over gold based catalysts [36–39]. Commercial imidazolium-based ILs (BMIMPF_6 and BMIMOTf) are used as benchmark ILs since they are among the most studied ILs in the literature and are compared to a Deep Eutectic Solvent prepared from choline chloride and urea [21,40]. The effect of the addition of 1-methylimidazole (MIM), an extra stabilizing agent is also studied. MIM is a precursor of the imidazolium salts and it was proposed by Dash and Scott [41] that it may play a role in the NPs stabilization as an IL impurity. The addition of polyvinylpyrrolidone (PVP) is also studied since this polymer is generally used in colloid preparation for its bulkiness and its ability to bind weakly to the NPs surface thus preventing their aggregation [42].

2. Experimental

2.1. Chemicals

1-Butyl-3-methylimidazolium hexafluorophosphate, BMIMPF_6 , (99.5%) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate, BMIMOTf , (99.5%) (Scheme 1a) were obtained from Solvionic and kept under argon on a molecular sieve before use. Titania (P25, 50 m^2/g) was purchased from Evonik. Urea (high purity grade, Amresco), acetonitrile (HPLC grade, Merck) and 1-methylimidazole (Scheme 1b) were used as received. Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%)



Scheme 1. Chemical structures of (a) the imidazolium-based ionic liquids BMIMPF_6 and BMIMOTf and of the stabilizing agents (b) MIM and (c) PVP.

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