

Synthesis and characterization of catalytic iridium nanoparticles in imidazolium ionic liquids

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Abstract

The reduction of $[\text{Ir}(\text{cod})\text{Cl}]_2$ (cod = 1,5-cyclooctadiene) dissolved in 1-*n*-butyl-3-methyl tetrafluoroborate, hexafluorophosphate and trifluoromethane sulphonate ionic liquids in the presence of 1-decene by molecular hydrogen produces Ir(0) nanoparticles. The formation of these nanoparticles follows the two-step $[\text{A} \rightarrow \text{B}, \text{A} + \text{B} \rightarrow 2\text{B} (k_1, k_2)]$ autocatalytic mechanism. The same mean diameter values of around 2–3 nm were estimated from in situ TEM and SAXS analyses of the Ir(0) nanoparticles dispersed in the ionic liquids and by XRD of the isolated material. XPS and EXAFS analyses clearly show the interactions of the ionic liquid with the metal surface demonstrating the formation of an ionic liquid protective layer surrounding the iridium nanoparticles. SAXS analysis indicated the formation of an ionic liquid layer surrounding the metal particles with an extended molecular length of around 2.8–4.0 nm depending on the type of the anion.

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1. Introduction

The stability of soluble transition-metal nanoparticles relies mainly on the steric and/or electronic protection provided by different types of water or organic solvent soluble stabilizers such as surfactants, polymers, quaternary ammonium salts, polyoxoanions, etc. [1–3]. In both models the slowing of the nanoparticle agglomeration rate is essentially due to the kinetic stabilization provided by a layer of surface-adsorbed anions or polymers [4,5]. The positive charge on the metal surface is ultimately induced by the adsorption of the anions to the coordinatively unsaturated, electron-deficient, and initially neutral metal surface [6,7]. In these cases the anion effect should be predominant in the formation, stabilization and properties of the nanoparticles. Indeed, the fundamental importance of surface-adsorbed anions in transition-metal nanoparticles has

been recently elegantly addressed and an “anion series” of relative nanoparticle formation and stabilization abilities for Ir(0) has been devised employing five different criteria [6]. Among these criteria the experimental confirmation that the anions coordinate to the metal surface and a well-defined nanoparticle formation reaction (nanoparticle formation mechanism) are the most important and difficult to achieve [6].

It was recently demonstrated that the catalytic properties of Rh nanoparticles are strongly influenced by the nature of the surfactant counter-anion [8]. In the same line, the catalytic activity of Ir nanoparticles is extremely sensitive to the nature of the capping ligand and ligand coverage. Thus, good capping ligands—that stabilize robust nanocrystals with very narrow size distributions—are almost inactive catalysts for the hydrogenation of olefins [9].

It has been recently reported that ionic liquids are a suitable medium for the preparation and stabilization of various transition-metal nanoparticles [10–27]. Although the intrinsic high charge of these salts, creating an electrostatic colloidal-type protection (analogous to the DLVO theory that is usually

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employed to rationalize the stabilization effect of classical quaternary ammonium salts [28] for transition-metal nanoparticles) may in principle account for the “stabilization” properties of the ionic liquids, no direct experimental evidence has been produced so far. Moreover, imidazolium salts differ in various aspects from classical quaternary ammonium salts. Imidazolium ILs are usually the major component of the mixture and possess pre-organized structures through mainly hydrogen bonds [29,30] that induce structural directionality in opposition to classical quaternary ammonium salts in which the aggregates display mainly charge-ordering structures [31]. Imidazolium ILs form an extended hydrogen bond network in the liquid state and are consequently highly structured, i.e., they can be described as “supramolecular” fluids [29,32–34]. It is noticeable that the anions and cations form aggregates of the type $[(\text{BMI})_x(\text{X})_{x-n}]^{n+}[(\text{BMI})_{x-n}(\text{X})_x]^{n-}$ where BMI is the 1-*n*-butyl-3-methylimidazolium cation and X is the anion, even in the gas phase [30]. Therefore, it is quite probable that the anion coordination to the nanoparticle surface in imidazolium ILs occurs via anionic aggregates of the type $[(\text{BMI})_{x-n}(\text{X})_x]^{n-}$ rather than isolated X anions. Therefore the DLVO model cannot be used in these systems as recently pointed out by Finke and Ott [4] since the DLVO model was not designed to account for counterions with multiple charges nor was is designed to account for sterically stabilized systems [35,36].

Moreover, it has been recently demonstrated that Ir(0) nanoclusters may react with imidazolium-based ILs to form surface-attached carbenes [37]. However, there are no in-depth studies pertaining to the influence of the ionic liquid counter-anion on the formation, stabilization and catalytic properties of transition-metal nanoparticles. Noteworthy, imidazolium ionic liquids [38–41] possess negligible vapor pressure and it is thus possible to investigate in situ their properties by physical chemical techniques that require high vacuum such as transmission electron microscopy (TEM) [21]. Moreover, the Ir(0) nanoparticles prepared in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid possess a small and narrow size distribution and are stable catalysts for the hydrogenation of alkenes and arenes [23]. Therefore this system, i.e., the Ir(0) nanoparticles prepared in imidazolium ionic liquids, constitutes a suitable and a rare case for a more general and in-depth investigation of the influence of the anions on the formation, stabilization and catalytic properties of such nanoparticles. The main goal of this work was to investigate the role of the counter-anion of the imidazolium ionic liquid on the formation and stabilization of Ir(0) nanoparticles. For these purposes we have investigated the kinetics of the formation of Ir(0) nanoparticles from the reduction of $[\text{Ir}(\text{cod})\text{Cl}]_2$ (cod = 1,5-cyclooctadiene) dispersed in 1-*n*-butyl-3-methylimidazolium (BMI)-based ionic liquids containing three anions with different basicities (BF_4^- , PF_6^- , and CF_3SO_3^-) with molecular hydrogen in the presence of 1-decene. The obtained Ir(0) nanoparticles dispersed in the ionic liquids were investigated by in situ TEM, EXAFS, and SAXS. The nanoparticles were isolated from the ionic liquids and analyzed by TEM, DRX, and XPS.

2. Results and discussion

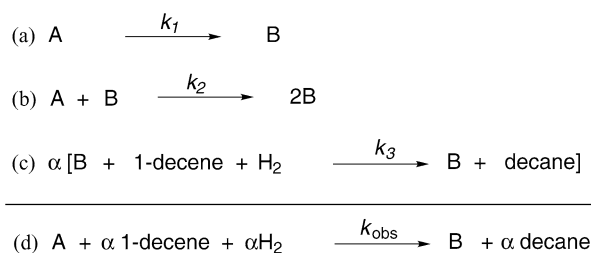
2.1. Formation kinetics of the Ir(0) nanoparticles

To monitor the formation of Ir(0) nanoclusters we employed an indirect method developed by Watzky and Finke [42]. The Ir(0) nanocluster mediated catalytic hydrogenation (H_2 uptake) activity is used as a reporter reaction via the *pseudoelementary* step concept, Scheme 1 (where A is the precatalyst and B is the catalytic active Ir(0) nanoclusters). If 1-decene hydrogenation (Scheme 1, Eq. (c)) is a fast reaction, on the time scale of steps (a) and (b), it can serve as a reporter reaction for the Ir(0) formation, i.e., the kinetics of the overall reaction are those represented only by Eqs. (a) and (b) (Scheme 1). Moreover, the sum of all three steps leads to a “kinetically equivalent” elementary step which relates the overall H_2 consumption stoichiometry (1-decene) with the formation of Ir(0) nanoparticles, the so-called *pseudoelementary* step (Eq. (d), Scheme 1).

The hydrogenation kinetics curves of 1-decene by $[\text{Ir}(\text{cod})\text{Cl}]_2$ dispersed in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄) and 1-*n*-butyl-3-methylimidazolium trifluoromethane sulphonate (BMI-CF₃SO₃) ionic liquids are shown in Fig. 1. These sigmoidal kinetics curves are characteristic of transition-metal nanocluster formation under reductive conditions.

The kinetics curves were treated using the *pseudoelementary* step and fitted by the integrated rate equation (1), for nucleation ($\text{A} \rightarrow \text{B}$, k_1) and autocatalytic surface growth ($\text{A} + \text{B} \rightarrow 2\text{B}$, k_2). For a more detailed description of the use of *pseudoelementary* step for the treatment of kinetic data and derivatization of the kinetic equations see elsewhere [43,44].

The obtained values for the nucleation and autocatalytic growth constants k_1 and k_2 are summarized in Table 1. The good fitting of the observed sigmoidal-shaped kinetic curves is a good indication of the formation of small size Ir(0) nanoparticles under our reaction conditions. Note that these of k_1/k_2



Scheme 1.

Table 1

Kinetic constants, k_1 and k_2 , obtained on the hydrogenation of 1-decene by the catalyst precursor $[\text{Ir}(\text{cod})\text{Cl}]_2$ dispersed in ionic liquids

Ionic liquid	k_1 (h^{-1})	k_2 ($\text{M}^{-1} \text{h}^{-1}$) ^a
BMI-PF ₆	2.04 ± 0.05	$3.2 \times 10^{-3} \pm 0.2 \times 10^{-3}$
BMI-BF ₄	0.14 ± 0.02	$1.2 \times 10^{-4} \pm 0.2 \times 10^{-4}$
BMI-CF ₃ SO ₃	0.35 ± 0.03	$1.0 \times 10^{-3} \pm 0.1 \times 10^{-3}$

^a Rate constant obtained considering the scalonement factor (1215, corresponding to substrate/catalyst ratio).

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