



Advanced nanostructured catalysts for hydroboration



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ABSTRACT

Metal nanocrystals have been prepared in onium salts using supercritical carbon dioxide assisted synthesis. During the process, metal salts precursors are reduced by H₂ in an organic solvent free media, the onium salts allowing both the stabilization of the nanostructured material and the preparation of an air and moisture stable powder made of embedded metal nanocrystals. Those catalysts proved to be highly effective in the hydroboration of alkyne process.

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1. Introduction

In many ways, hydroboration [1] remains one of the key reactions used in modern synthetic chemistry to selectively functionalize insaturations [2]. When performed on carbon–carbon triple bonds, the resulting vinylboranes can be subsequently used in various transformations, including transition metal catalyzed cross-coupling. To promote this reaction, numerous homogeneous catalytic systems have been developed, mostly based on late transition metal complexes [3]. Group-IV metal (Ti, Zr) [4] were proved to be efficient as well. In order to apply this versatile chemistry at a larger scale, heterogeneous catalysts are required. However, due to reactivity and selectivity issues, only few heterogeneous systems have so far been developed. For homogenous complexes immobilization several approaches are described. Using fluorinated tagged ligand, rhodium complexes can be trapped in a perfluorinated solvent, efficiently promoting the hydroboration for several cycles [5]. A very nice approach has been used by Fernandez et al. [6] to intercalate cationic rhodium complexes in montmorillonite interlayers. Even if they mostly studied alkene hydroboration, this example is one of the most efficient systems to recycle hydroboration catalyst. Recently a copper-catalyzed vinylboronate formation was disclosed using bis(pinacolato)diboron as a boron source [7].

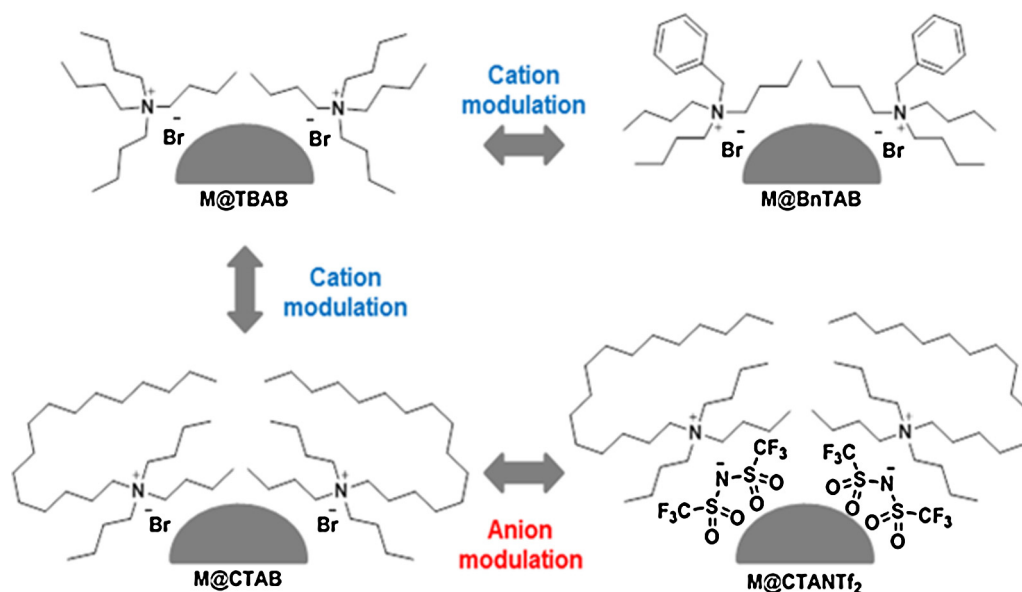
Although the reagents/product are similar, the reaction mechanism is different and is supposed to involve a syn-addition of the borylsodium onto the triple bond [7]. This reaction is somehow related to the gold nanoparticles (NPs) catalyzed diboration of alkynes showing firstly that NPs could promote carbon–bond formation [8]. Finally, it has recently been found that iridium nanoparticles favor hydroboration of alkene and alkyne [9].

Despite the large use of hydroboration to yield valuable building blocks, no general studies have been reported on transition metal nanoparticles (NPs)/nanocrystals (NCs) catalyzed hydroboration. This could be a first step toward the design of an active bulk heterogeneous catalyst.

With this work we would like to show/demonstrate how the use of onium salts (OSs) combined with supercritical carbon dioxide (scCO₂) technology has enabled the preparation of a vast variety of metal nanocrystals stabilized by OSs as good nanocatalysts for hydroboration (Scheme 1). For semi-heterogeneous catalysis, the surface state is critical in order to obtain a good catalytic activity. Hence, we developed a method for organic solvent free preparation of NCs embedded in OSs. Previously, we have shown that a powder of onium salt containing palladium NPs could be obtained by simply mixing trimethylbutylammonium hexafluorophosphate ([tmba]PF₆) with a palladium salt above the onium salt melting point (m.p. 176 °C) [10]. This concept is generalized herein by using other metal precursors (Rh, Ir, Pt, Ru) and OSs with lower or very high melting points. In all cases, the use of supercritical fluids, supercritical carbon dioxide in our case, was crucial. Indeed, among numerous properties displayed by supercritical fluids, we

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Scheme 1. Sketch of hybrid organic/inorganic NCs, M@OS labeled as M@TBAB, M@BnTAB, M@CTAB and M@CTANTf₂ obtained by onium salts cation/anion modulation.

have used the high solubility of scCO₂ in liquid OSs which enables the fast transport of metal salts inside the ionic phase.

2. Experimental

2.1. Materials and methods

The metal organic precursors were purchased from Aldrich and Strem Chemicals and used as received: ruthenium (III) acetylacetonate (Ru(acac)₃, 97%), rhodium (II) trifluoroacetate dimer [Rh(tfa)₂]₂, 95%), chloro-1,5-cyclooctadiene iridium (I) dimer ([Ir(cod)Cl]₂, 99%) and platinum (II) hexafluoroacetylacetonate (Pt(hfa)₂, 98%). The onium salts were purchased from Aldrich as following: (a) tetrabutylammonium bromide (TBAB), (b) benzyltrimethylammonium bromide (BnTAB), (c) cetyltrimethylammonium bromide (CTAB). The cetyltrimethylammonium bis(trifluoromethyl-sulfonyl)imide (CTANTf₂) was prepared according to a previously reported methodology [11]. Phenylacetylene and pinacolborane were purchased from Alfa Aesar and used as received.

Final materials morphologies, labeled M@TBAB, M@BnTAB, M@CTAB and M@CTANTf₂ respectively (where M = Ru, Rh, Ir and Pt) were characterized by conventional (TEM-JEOL 2100) and high resolution (TEM-FEG HR-JEOL 2200FS) transmission electron microscopy. The samples were prepared by dissolving the powder hybrid nanocatalyst in an organic solvent (ethanol or acetone) and deposited by drop casting on a carbon grid.

Powder XRD analysis on the above mentioned systems were performed using an X-ray diffractometer with Cu $\lambda_{K\alpha}$ radiation (PANalytical X'Pert Pro). FTIR reflection measurements were made using a Bruker spectrophotometer working in the 7500–400 cm⁻¹ range.

All catalytic reactions were carried out under an argon atmosphere. ¹H NMR was recorded on Bruker Avance 300 FT 300 MHz spectrometers using CDCl₃ as internal reference. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz, respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. GC-MS analysis was performed with a HP 6890 series GC-system equipped with a J&W Scientific DB-1701 capillary column, a HP 5973 mass selective detector (EI) using the following

method: 70 °C for 1 min then 20 °C min⁻¹ until 230 °C then 6 min at 230 °C.

2.2. Synthesis procedure for nanocatalysts preparation

Synthesis in supercritical fluid media required a high pressure/high temperature home-made stirred batch reactor (made of stainless steel), with a volume of 60 mL. Reaction parameters (pressure and temperature) were monitored with a pressure sensor inside the reactor and an external heating mantle coupled with a thermocouple placed inside the reactor.

In the reactor were mixed the onium salt with the metal precursor (1 wt% metal) both in powder form. Using gas bottle containing a mixture of CO₂ + H₂ in volume ratio 80:20 we first loaded 3.4 bar of this mixture. During heating (100 ≤ T ≤ 185 °C), CO₂ was loaded within the reactor through a high pressure pump to reach the desired pressure of 230 bar. The set temperature and pressure were maintained constant for 30 min, when the chemical reaction takes place. At the end of reaction, the reactor was depressurized and CO₂ vented through the reactor for few more minutes as cleaning and drying steps. The final product, nanocrystals embedded in the solid matrix of ammonium salt was recovered as dark powder and used directly in the hydroboration reaction. A sketch of the experimental setup is presented elsewhere [12].

As metal precursors, Ru(acac)₃, [Rh(tfa)₂]₂, [Ir(cod)Cl]₂ or Pt(hfac)₂, commonly employed for the nanostructured material fabrication in supercritical fluids media, were used [13]. The materials prepared by the above described procedure and the experimental parameters used are listed in the following Table 1. Upon reduction, the counteranion is protonated leading to

Table 1

Precursors and reaction temperatures used for the preparation of M@OS nanocatalysts, where OS = TBAB, BnTAB, CTAB and CTANTf₂ and M = Pt, Ir, Rh and Ru.

Precursor type	T _r (°C)	scCO ₂ – 230 bar/30 min			
		TBAB	BnTAB	CTAB	CTANTf ₂
Ru(acac) ₃	185	Ru@TBAB	Ru@BnTAB	Ru@CTAB	Ru@CTANTf ₂
[Rh(tfa) ₂] ₂	150	Rh@TBAB	Rh@BnTAB	Rh@CTAB	Rh@CTANTf ₂
[Ir(cod) ₂ Cl]	100	Ir@TBAB	Ir@BnTAB	Ir@CTAB	Ir@CTANTf ₂
Pt(hfac) ₂	100	Pt@TBAB	Pt@BnTAB	Pt@CTAB	Pt@CTANTf ₂

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