Electrochimica Acta 122 (2014) 289–295

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Palladium nanoparticles–polypyrrole composite as an efficient catalyst for cyanation of aryl halides

Tatiana V. Magdesieva[a,*], Oleg M. Nikitin[a,b], Ekaterina V. Zolotukhina[c], Mikhail A. Vorotyntsev[a,c,d]

[a] Department of Chemistry, M.V. Lomonosov Moscow State University, Moscow, Russia
[b] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science, Vavilova Str. 28, 119991, Moscow, Russia
[c] Institute for Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia
[d] ICMUB-UMR 6302, CNRS - University of Burgundy, Dijon, France

ARTICLE INFO

Article history:
Received 6 June 2013
Received in revised form
26 September 2013
Accepted 28 September 2013
Available online 18 October 2013

Keywords:
Nanocomposite
Polypyrrole
Palladium nanoparticles
Catalysis
Supported catalysis

ABSTRACT

New palladium-polypyrrole (Pd/PPy) nanocomposites have been studied in cyanation of aryl halides with $K_4Fe(CN)_6$ and showed high catalytic efficiency. Aryl iodides, bromides, and chlorides are active. The reaction can be performed both in organic solvents and in water; in the latter case, the catalyst was immobilized on graphite support. The cyanation of inactivated aryl chlorides is of special importance as only a few publications dealing with efficient cyanation of aryl chlorides are available, in which expensive and poisonous phosphine ligands and non-aqueous solvents are used. The influence of the morphology of the catalyst on its efficiency in cyanation was investigated, and it was revealed that PPy spheres of about 30 nm in diameter with palladium nanoparticles of 1.2 nm in size are more efficient than bigger polymer ones (about 60 nm in diameter). Palladium content in polypyrrole spheres does not influence the yield of nitriles.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Cyanation of aryl halides, ArHal, is one of the very important and widely used reactions since benzonitriles, ArCN, are building blocks for various pharmaceuticals, herbicides, dyes, etc. [1–4]. A nitrile substituent is also an important precursor for numerous chemical transformations yielding other functional groups. Various approaches to synthesis of benzonitriles are known. The most widely used traditional method is cyanation of aryl halides or aryl diazonium salts with copper(I) cyanide [5]. A useful alternative for preparation of substituted benzonitriles is palladium-catalyzed cyanation of aryl halides (usually, iodides or bromides) with cheap but toxic cyanides of alkaline metals or zinc. A complete review of the evolution of palladium-catalyzed cyanation of aryl halides is given in [6], with detailed discussion of advantages and drawbacks of each method. In particular, one can see that the palladium-catalyzed cyanation of aryl bromides and iodides works well with various palladium catalysts and cyanide sources.

Recently, a new cyanating agent for aryl halides, hexacyanoferrate(II), $K_4Fe(CN)_6$, was described [7] (see also [8] for an overview). Advantages of this reagent as compared to the traditional approaches are quite obvious and very significant. First of all, $K_4Fe(CN)_6$ is non-toxic, contrary to cyanides. Second, all cyanide ions on the iron(II) center can be transferred to the aryl halide and this is in line with the atom-economy strategy which is one of the key requirements of sustainable chemistry [9,10]. The general problem of cyanation is deactivation of the transition metal catalysts due to formation of stable cyanide complexes [11]. A slow release of cyanide ions in the case of $K_4Fe(CN)_6$ allows one to improve the catalyst productivity.

The properties mentioned above make this reagent very prospective for synthetic applications. Its utilization requires catalysis with palladium species [7]; usually, palladium complexes with various phosphine ligands are used. The influence of various electron-rich and sterically hindered ligands on the efficiency and selectivity of cyanation was investigated [12]. Though a number of inactive aryl chlorides (including chloroanilines and chlorophenols) have been successfully converted to nitriles [11–15], it requires a prolonged heating at high temperatures, and the presence of rather complex and poisonous phosphine ligands.

A novel palladium complex with trans-spanned bidentate phosphine ligand insensitive to the steric hindrance of substrates has

---

* Corresponding author. Tel.: +74959393065.
E-mail addresses: tvm@org.chem.msu.ru (T.V. Magdesieva), mivo2010@yandex.com (M.A. Vorotyntsev).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.09.157

been described recently [16]. Very good-to-excellent yields of ortho-substituted benzonitriles were obtained; the reaction can be performed in mild conditions (90 °C) and it circumvents the need for inert atmosphere but, unfortunately, only aryl bromides are active. In spite of essential benefits, a significant disadvantage of the protocols using phosphine complexes of palladium as catalysts is possible release of toxic phosphines as byproducts of the reaction. Ligand-free cyanation with $K_4Fe(CN)_6$ by means of palladium acetate, $Pd(OAc)_2$, has also been tested but it was efficient only for aryl bromides [17] and activated aryl chlorides [6]. Pd/C catalyzed cyanation of aryl bromides with hexacyanoferrate(II) [18] gave benzonitriles in good-to-excellent yields. Furthermore, Pd/C can be recycled by simple filtration without significant decrease in catalytic efficiency.

Utilization of water as solvent in transition-metal-catalyzed reactions is very prospective. It often facilitates the workup procedure, allows one to avoiding toxic solvents and stays in line with green chemistry tendencies. However, only a few publications on cyanation with hexacyanoferrate in water are yet available [19,20] and all are limited to active aryl halides only. Recently, palladium-catalyzed cyanation of aryl mesylates in water were reported [21]. The reaction can be performed at 80 °C and these conditions may be considered as the mildest ever reported for the coupling of aryl mesylates, though the use of complicated phospine ligands should be mentioned.

Tremendous growth of the number of publications describing various types of nanocatalysts during the recent years clearly indicates that this area opens interesting possibilities for catalysis and possesses significant advantages [22–26]. Recently, palladium nanoparticles supported on nanocrystalline copper(II) oxide (CuO) were tested in cyanation of aryliodides with $K_4Fe(CN)_6$ and showed high efficiency [27]. However, cyanation poisons the catalyst and it is not recyclable. Only aryl iodides are active under the reaction conditions, while other halides remain inert. A new recyclable catalytic system based on palladium nanoparticles stabilized by a copolymer of *N*-vinylimidazole with *N*-vinylcaprolactam was developed in [28] but it turned out to be applicable for cyanation with $K_4Fe(CN)_6$ of arylbromides only. Palladium containing nanostructured silica bearing trialkyl-(4-pyridyl)-ammonium binding sites were tested in cyanation in dimethylformamide, DMF, in the presence of triethylamine as a base but it worked for aryliodides only [29]. It has been concluded recently on the basis of kinetic studies of cyanation reactions that their catalysis was performed by palladium metal nanoparticles generated from the initial solute molecular palladium complex under reaction conditions [30]. High yields of nitriles were obtained even for aryl chlorides but the catalytic system applied requires toxic phosphine ligands.

Thus, the analysis of literature data reveals that creation of palladium catalyst without toxic ligands which would be efficient for cyanation of cheap and available aryl chlorides, including electron-rich ones, eligible for aqueous solutions and recyclable is still a challenge. This situation stimulated us to undertake investigation of a new ligand-free nanosize palladium catalyst in cyanation of arylhalides with $K_4Fe(CN)_6$.

Recently, we described a simple non-template one-step method for synthesis of palladium nanoparticles encapsulated into a polypyrrole shell via direct redox reaction between tetraamminepalladium(II) dichloride, $Pd(NH_3)_4Cl_2$, and pyrrole in aqueous medium [31,32]. The formation of nanocomposite catalysts via redox-polymerization of a heterocyclic precursor under action of metal ions is one of the approaches promising for catalytic application. It allows avoiding addition of surface stabilizers (which are often used for preparation of stable nanosize systems) since formed conducting polymer matrix stabilizes nanoparticles itself and prevents their aggregation. Formation of the surface free of adsorbates increases the catalytic activity of palladium nanoparticles. The inherent reactivity of unligated palladium is considered to be sufficient for oxidative addition for most kinds of C-X bonds [28,33], while ligandless palladium often performs catalysis more efficiently than its ligand-modified counterpart [34–38]. In this context palladium-polypyrrole nanocomposite, Pd/PPy, seems to be a promising candidate.

Pd/PPy nanocomposite was initially tested as catalyst for Suzuki–Miyaura and Sonogashira couplings and it showed high efficiency [32,39]. In the present work we describe the application of Pd/PPy nanocomposites as catalysts for cyanation of various aryl halides with $K_4Fe(CN)_6$ in organic solvents and in aqueous medium. The influence of structural features of the Pd/PPy composite (diameter of PPy shells and palladium content in the globule) on the catalytic activity will also be examined.

2. Experimental

2.1. Substances

N-methylpyrrolidone (NMP, Aldrich, spectroscopic quality) was stirred over calcium hydride, CaH_2, for 3 h. and distilled under reduced pressure. Acetonitrile (AN, Aldrich, spectroscopic quality, <0.02% water content) was refluxed over CaH_2 for 12 h and distilled. Water was distilled using aquadistillator BE-4 (Russia) for catalytic experiments. Aryl halides were commercially available from Aldrich and Acros Organics: iodobenzene, PhI, 99% Aldrich, bromobenzene, PhBr, ≥99.5% (Aldrich), chlorobenzene, PhCl, 99.8% (Sigma–Aldrich), 1-bromo-4-nitrobenzene, $4\text{-}NO_2C_6H_4Br$, 99% (Aldrich), 1-chloro-4-nitrobenzene, $4\text{-}NO_2C_6H_4Cl$, 99% (Aldrich), 1-chloro-2,4-dinitrobenzene, $2,4\text{-}(NO_2)_2C_6H_3Cl$, ≥99% (Aldrich), 4-bromotoluene, $4\text{-}CH_3C_6H_4Br$, 98% (Aldrich), 4-chlorophenol, $4\text{-}HOC_6H_4Cl$, ≥99% (Aldrich), 4-bromobenzonitrile, $4\text{-}NCC_6H_4Br$, 99% (Aldrich), 4-bromoanisole, $4\text{-}CH_3OC_6H_4Br$, 98% (Acros Organics), 1-chloro-4-iodobenzene, $4\text{-}IC_6H_4Cl$, 99% (Acros Organics), 2-bromopyridine, 99% (Aldrich), 2-chloropyridine, 99% (Aldrich), sodium carbonate, Na_2CO_3, 98% (Reachem), potassium phosphate, K_3PO_4, 98% (Reachem). Pyrrole, 98+% (Alfa Aesar), was distilled under inert atmosphere. Tetraamminepalladium(II) chloride monohydrate, $Pd(NH_3)_4Cl_2{\cdot}H_2O$, 99.9% (Alfa Aesar) was used as supplied.

2.2. Preparation and characterization of Pd/PPy nanocomposites [31,32]

In typical synthesis, equal volumes (250 ml) of initial aqueous solutions of 2 mM of $Pd(NH_3)_4Cl_2$ monohydrate and of pyrrole monomer (20 mM or 600 mM) were mixed. The corresponding mixed solutions are denoted as 1:10 and 1:300, respectively, in accordance with their milliMolar concentrations. The color of the mixture changed from light brown to dark brown due to colloid formation in the first hour after starting the reaction. Progressive darkening of the solution occurred. The reaction mixture was stirred in ultrasonic bath ($T = 50\,^\circ C$) for 5 h per day during the first 5 days, then the reaction mixture was kept without ultrasonification for the next 5 days until colloid sedimentation took place. The obtained dark precipitate was rinsed several times with water and acetonitrile until the effluent became colorless (UV–vis controlled) and then it was dried under vacuum for 4 h. Pd/PPy composite was used without further treatment for characterization and catalytic tests.

The morphology of Pd/PPy materials was characterized by scanning electron microscopy, SEM, and transmission electron microscopy, TEM, techniques. For these experiments a portion of Pd/PPy powder was dispersed in ethanol under ultrasonic treatment. Then, a drop of obtained stable suspension was placed

Download English Version:

https://daneshyari.com/en/article/186321

Download Persian Version:

https://daneshyari.com/article/186321

Daneshyari.com