Dyes and Pigments 92 (2012) 1308–1313

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

Nanoparticles of organosilane-based nitrite ionic liquid immobilized on silica for the diazotization of aniline derivatives and subsequent synthesis of azo dyes

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ARTICLE INFO

Article history:
Received 20 July 2011
Received in revised form
14 September 2011
Accepted 20 September 2011
Available online 28 September 2011

Keywords:
Azo-coupling
Azo dyes
Diazotization
Nitrite ionic liquid
Immobilized ionic liquid
Nanoparticle

ABSTRACT

Imidazolium based nitrite ionic liquid containing trimethoxysilyl group was prepared from the reaction of N-methylimidazole and (3-chloropropyl) trimethoxysilane. This ionic liquid was immobilized on silica covalently to give nanoparticles with the imidazolium nitrite moiety remaining intact. The diazotization reaction was performed as a model reaction to examine the activity of these nanoparticles as a nitrosonium source. Excellent performance was exhibited in the diazotization reaction of various aniline derivatives in the presence of HCl under mild heterogeneous conditions (room temperature and short reaction time). In-situ coupling of diazonium salts to a range of tertiary anilines, phenols and naphthols afforded the requisite azo dyes in good yield, using standard experimental procedures.

1. Introduction

Organosilanes containing covalently bonded catalyst were used as a linker or coupling agent to an oxide support. The complexes of metals with organosilane-based ligands were synthesized and immobilized on the oxide supports [1]. Organosilane-based *N*- heterocyclic carbene–palladium complex immobilized on silica particles was reported as a catalyst for the Suki reaction [2]. Ionic liquids are growing in importance over the past few years due to their unique physical and chemical properties [3]. Ionic liquids containing a functional group which is covalently tethered to its cation or anion, TSILs, have been increasingly used as solvents and reagents or catalysts due to their specific properties [4–9].

Very recently we used nitrite functionalized ionic liquid as a nitrosonium source for the diazotization reaction of a variety of aniline derivatives [10]. Ionic liquids immobilized on metal oxides such as silica was used as catalyst in some organic reactions [11–14]. Sugimura and co-workers synthesized the immobilized acidic ionic liquids by copolymerization with styrene and used them as catalyst for the acetal formation [15]. Diphenylmethane and its derivatives were synthesized using immobilized chloroferrate ionic liquid as an efficient and reusable catalyst [16].

Diazoniums are an important group of organic compounds which have interesting applications in synthetic organic chemistry. These compounds can be reduced into radicals and used for the covalent surface modification of carbon [17], metal [18], and semiconductors [19]. Diazoniums also have been used for the preparation of the important synthetic azo dyes via well-known azo-coupling reaction [20–22]. Nitrous acid is well-known reagent for the diazotization of aniline derivatives under acidic conditions. Many methods have been reported for the diazotization and subsequent azo-coupling reaction [23–31].

In continuation of our work on the using of task-specific nitrite ionic liquid (IL-ONO) as solvent and reagent for the diazotization and synthesis of azo dyes [10], we now introduce nitrite ionic liquid immobilized on silica as a new reagent that can act as a nitrosonium source for the efficient conversion of aryl amines to their corresponding diazonium salts. In-situ azo-coupling of these diazonium salts afforded the related azo dyes in good yields.

2. Experimental

2.1. General information

All reagents were purchased from Merck Company and used without further purification. Infrared spectra were recorded in KBr and were determined on a Perkin Elmer FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance AC-400 MHz using

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doi:10.1016/j.dyepig.2011.09.013

DMSO-d_6 or $CDCl_3$ as the deuterated solvents and TMS as internal standard. All melting points measured in open glass-capillaries using a Stuart melting point apparatus.

2.1.1. Synthesis of 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride

1-Methylimidazole (20 mL, 0.25 mol) and (3-chloropropyl) trimethoxysilane (6.04 g, 0.25 mmol) were refluxed at 80 °C for three days in the absence of any catalyst and solvent. The unreacted materials were washed by diethyl ether (3 × 8 mL). The diethyl ether was removed under reduced pressure at room temperature, followed by heating under high vacuum, to yield a yellowish viscous liquid. Isolated yield was 98%. FT-IR (KBr, cm^{-1}): 1656, 1612, 1584. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm): 10.22 (broad, 1H, Ar–H), 7.59 (1H, dd, $J = 7.89$ and 2.86 Hz, Ar–H), 7.26 (1H, dd, $J = 7.89$ and 2.79 Hz, Ar–H), 4.06 (2H, t, $J = 7.25$ Hz, $-NCH_2$), 3.86 (3H, s, $-NCH_3$), 3.30 (9H, s, OCH_3), 1.74 (2H, tt, $J = 7.14$ Hz, $-CH_2$), 0.37 (2H, t, $J = 7.09$ Hz, $SiCH_2$).

2.3. Synthesis of silica nanoparticles

Ammonia solution 25% (750 μL, 10 mmol) and water (1.98 mL) were added into a 250 mL round bottom flask containing absolute methanol (100 mL). The solution is stirred for 10 min at room temparature. While stirring of the solution, tetraethoxysilane, TEOS (10.41 g, 500 mmol) was added dropwise. The final solution is stirred *continuously* for three days at ambient temperature. The particle size was examined under scanning electron microscopy.

2.4. Procedure for the immobilization of chloride ionic liquid onto silica nanoparticles

The silica nanoparticles suspension are precipitated with n-hexane and extracted through centrifugation (twice at 6000 rpm) before being re-suspended in dichloromethane. Silica (1.016 g) was suspended in CH_2Cl_2 (5 mL) and the solution of 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride (300 mg, 0.929 mmol) in CH_2Cl_2 was then added. The mixture was stirred for 3 days at 40–50 °C. In the following step, the solvent and the methanol created in the grafting step were distilled off and the remaining solid dried under high vacuum and the excess of 1-methyl-3-(3-trimethoxy silylpropyl) imidazolium chloride removed by extraction with boiling dichloromethane. After drying of residue under vacuum at room temperature, the nanoparticles of immobilized chloride ionic liquid on to silica was prepared.

2.5. Anion exchange in the immobilized ionic liquid

Immobilized chloride ionic liquid **6** and an excess amount of $NaNO_2$ were added into the deionized water and stirred for 24 h at room temperature. NaCl which was prepared during the exchange of chloride anion with NO_2, was removed by washing the mixture with deionized water (3 × 30 mL). Immobilized nitrite ionic liquid was obtained typically in 98% yield as a white powder (Scheme 2). Immobilized nitrite ionic liquid nanoparticles were examined under scanning electron microscopy.

Comparing of the IR spectra of chloride ionic liquid **5** and nitrite ionic liquid **8** showed that a broad bond signal at 1349 cm^{-1} was appeared in the spectrum of nitrite ionic liquid which was not observed in the spectrum of chloride ionic liquid. This difference was also observed comparing the two IR spectra of immobilized chloride ionic liquid **6** and immobilized nitrite ionic liquid **7** and a broad bond signal at 1335 cm^{-1} was appeared in the spectrum of ionic liquid 7.

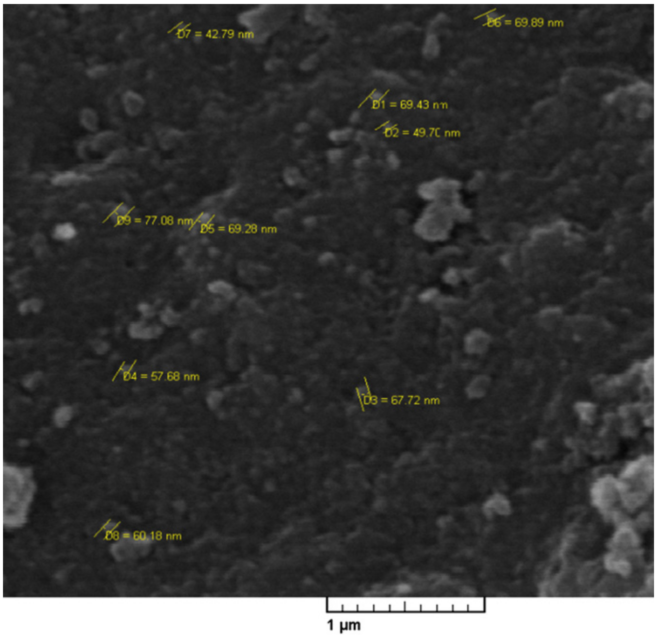

Fig. 1. The SEM image of immobilized nitrite ionic liquid 7.

2.6. Diazotization using pure nitrite ionic liquid 8, general procedure

Aniline derivative (20 mmol) was dissolved in 10 mL of 37% HCl. The mixture was stirred at 0–5 °C for 35 min. Pure nitrite ionic liquid (25 mmol) was added to aniline solution. Diazonium salt product was assayed by well-known azo-coupling reaction of phenol or aniline derivatives. For the coupling reaction with phenolic compounds, the reaction mixture was continuously added to the solution of phenolic compound (20 mmol) and NaOH (1 g) in 10 ml water. The participated dyes were filtered off and washed three times with cold water to afford the crude azo dyes. The crude

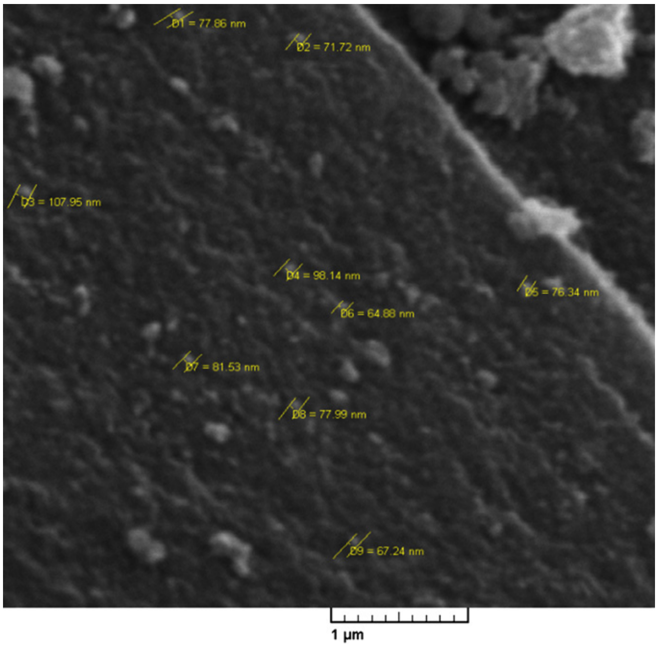

Fig. 2. The SEM image of silica nanoparticles.