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Ionic liquid and ethyl-based bifunctional ordered nanoporous organosilica supported palladium: An efficient catalyst for homo-coupling of phenylacetylenes

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ABSTRACT

A novel bifunctional ordered nanoporous organosilica with ethyl and ionic liquid framework supported palladium (Pd@ILEt-BNOS) is prepared, characterized and its catalytic performance in the homo-coupling of phenylacetylenes is developed. The Pd@ILEt-BNOS was prepared *via* simultaneous hydrolysis and condensation of bis(triethoxysilyl)ethane and alkyl-imidazolium ionic liquid in the presence of structure directing agent followed by treatment with palladium acetate. This nanostructure was characterized using transmission electron microscopy (TEM), nitrogen adsorption-desorption analysis, scanning electron microscopy (SEM), low angle X-ray diffraction (LAXRD), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, thermal gravimetric analysis (TGA) and energy dispersive X-ray (EDX) analysis. The Pd@ILEt-BNOS was successfully applied as efficient catalyst in the homo-coupling of phenylacetylenes and gave corresponding products in excellent yield. This was recovered and reapplied seven times without importance decrease in its efficiency. The life-time and stability of the catalyst were also investigated under applied conditions.

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1. Introduction

Periodic mesoporous organosilicas (PMOs) are one of the most important family of hybrid organic-inorganic nanostructures with advantages of high-ordered structures, uniform pore size, homogenous distribution of organic bridges into a silica framework as well as high thermal and mechanical stability [1–3]. Dissimilar conventional organo-functionalized mesoporous silicas, PMOs offer the possibility to adjust their chemical and physical properties as well as their thermal and mechanical stability through the incorporation of different organic functional groups in their pore walls [3–6]. These advantages made PMOs to be highly attractive candidate for potential applications such as catalysis, adsorption, chromatography, electronics, metal adsorption, controlled drug release and immobilization or encapsulation of biomolecules [3–14]. To increase advantages of PMOs, especially in the field of catalysis, more recently a new family of these called bifunctional PMOs (BPMOs) composed of different bridging organic units in the mesoporous wall with versatile surface properties have been prepared and successfully applied in a number of chemical and material processes [15–17]. These nanostructured materials are prepared through hydrolysis and polycondensation of silsesquioxane precursors of the type $(R'O)_3Si\text{-}R\text{-}Si(OR')_3$, being R′ is usually methyl or ethyl groups and R the organic bridging group, in the presence of structure-directing agents [15–20]. To date different precursors based on phenyl, ethyl, thiophene, isocyanurate, sulfide bridges, *etc* have been used for the preparation of BPMOs [15–25]. An interesting and valuable precursors with unique chemical and physical properties is ionic liquid (IL). The IL-based BPMOs have advantages of both ionic liquids and ordered nanoporous materials and can be used as adsorbent and effective support for immobilization of different metal-based catalysts in the catalytic processes [26–31]. Realizing these facts and according to importance of Pd-containing mesostructures in catalytic processes [32,33], in the present study a novel ionic liquid and ethyl based bifunctional ordered nanoporous organosilica (ILEt-BNOS) is prepared and applied as efficient support for successful immobilization of palladium species. The prepared material was endowed with both ethyl and ionic liquid groups within its pore wall. In fact, the ionic liquid sites of the material are potentially applicable for successful support of metallic-sources *via* ion-exchange mechanism and/or electrostatic

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interaction. The incorporated ethyl moieties together with aliphatic parts of ILs also increase the lipophilicity of the designed nanostructure that is very important property in the organic processes. This palladium-containing ILEt-BNOS was characterized using several techniques and applied as powerful catalyst in the homo-coupling of phenylacetylenes [34–41].

2. Experimental section

2.1. Synthesis of ionic liquid and ethyl-based bifunctional ordered nanoporous organosilica (ILEt-BNOS)

Bifunctional ionic liquid and ethyl-based NOS (ILEt-BNOS) was prepared as following: potassium chloride (10 g) and pluronic P123 (2 g) were added in a flask containing distilled water (12.2 mL) and HCl (2M, 53.6 mL). The resulting mixture was stirred at 40 °C. After a homogeneous solution was obtained, a methanol solution of 1,3-bis(trimethoxysilylpropyl)imidazolium chloride (2.33 mmol), tetramethoxysilane (TMOS, 11.65 mmol) and 1,2-bis(triethoxysilyl) ethane (BTESE, 9.32 mmol) was added in the reaction vessel and stirred at 40 °C for 24 h. Then, the obtained mixture was statically heated at 100 °C for 72 h. The resulting material was filtered, completely washed with water/ethanol and dried at 60 °C. The P123 surfactant was removed by a Soxhelet apparatus using a solution of EtOH:HCl (100:3). The final nanostructure was dried at 80 °C for 12 h and denoted as ILEt-BNOS.

2.2. Preparation of palladium containing ILEt-BNOS (Pd@ILEt-BNOS) catalyst

For the preparation of Pd@ILEt-BNOS, firstly ILEt-BNOS (1 g) was added in dimethyl sulfoxide (DMSO, 15 mL) and it was stirred at room temperature. After complete dispersion of ILEt-BNOS, palladium acetate (2.5 mmol) was added and the resulting mixture was stirred at room temperature for 20 h and then at 60 °C for 2 h under argon atmosphere. This mixture was then filtered and washed completely with DMSO to remove unreacted palladium acetate. The final material was dried at 70 °C for 12 h and denoted as Pd@ILEt-BNOS. The loading of the palladium was obtained to be 0.55 mmol/g by the means of the Pd-content obtained from inductively coupled plasma/optical emission spectroscopy (ICP-OES).

2.3. Homo-coupling of phenylacetylenes in the presence of Pd@ILEt-BNOS

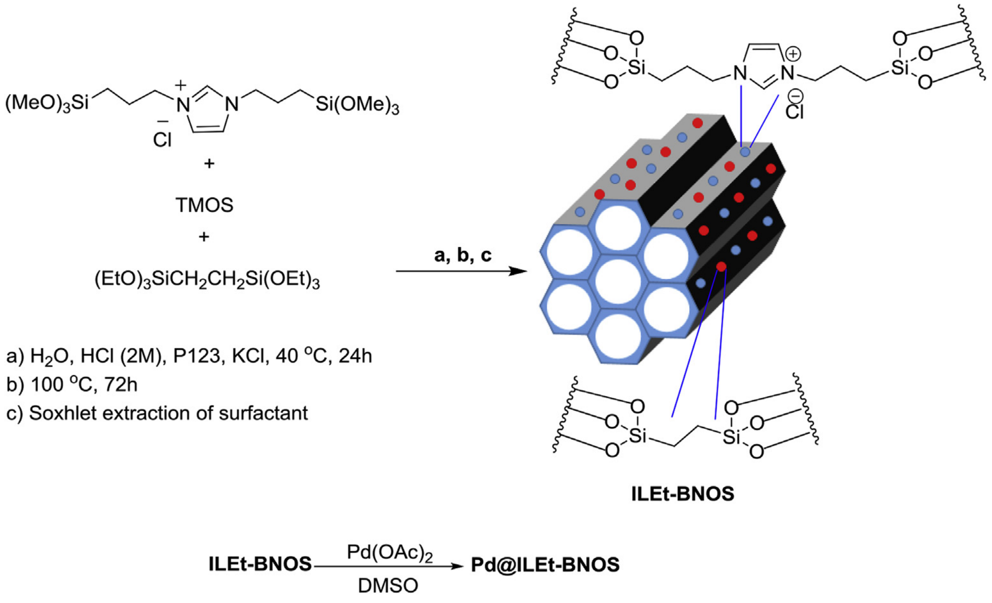
For this purpose, phenylacetylene (2 mmol), piperidine (2 mmol), CuI and 0.7 mol% of catalyst were added in EtOH (10 mL). The resulting mixture was stirred at 60 °C and the reaction progress was monitored using thin layer chromatography (TLC). After completing of the reaction, the obtained mixture was filtered and washed with hot ethanol. Then, some ice-species were added into filtrate to crystalize of the corresponding homo-coupling products.

3. Results and discussion

The preparation of the Pd@ILEt-BNOS was achieved *via* acid-catalyzed hydrolysis and co-condensation of bis(triethoxysilyl) ethane, tetramethoxysilane and 1,3-bis(3-trimethoxysilylpropyl) imidazolium chloride in the presence of pluronic P123 surfactant followed by treatment with palladium acetate according to Scheme 1.

The Pd@ILEt-BNOS was characterized by DRIFT to study the functionality of the material (Fig. 1S). The peaks observed at 700-770 cm^{-1} were assigned to symmetric vibrations of C-Si bonds. The symmetric and asymmetric stretching vibrations of Si-O-Si were cleared at 1100, 1043 and 947 cm^{-1}. The stretching vibrations of C=C and C=N of imidazolium rings were observed, respectively, at 1450 and 1633 cm^{-1}. The bands at 2926 and 3088 were, respectively, due to aliphatic and aromatic C-H stretching vibrations. The broad peak cleared at 3400 cm^{-1} was assigned to OH stretching vibrations of material surface.

Thermal gravimetric analysis (TGA) was also performed to study the thermal behavior of the material (Fig. 1). Three weight losses were observed in this analysis. The first one at temperature below 100 °C is assigned to removal of physically adsorbed water and ethanol or methanol solvents. The second weight loss between 100 and 250 °C is attributed to elimination of remained surfactant template. The main weight loss at temperature higher than 250 °C



Scheme 1. Preparation of Pd@ILEt-BNOS catalyst.

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