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Short Communication

Carbons supported bio-ionic liquids: Stability and catalytic activity

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ABSTRACT

[Chol][Pro] was supported on different porous carbon materials. Subsequently, the catalytic activity of the heterogeneous systems in the Michael reaction between cyclohexanone and β-nitrostyrene was studied. Excellent conversions and high diasteroselectivities were attained by supporting [Chol][Pro] on the heat treated mesoporous carbons. The stability of the [Chol][Pro] and consequently, its catalytic activity were strongly influenced by the textural and surface chemical properties of the carbon supports.

1. Introduction

Ionic liquids (ILs) are being applied as solvents and/or catalysts in organocatalysis [1]. The versatility of the ILs together to the huge number of synthetic alternatives offered by organocatalysis have lead to the development of several innovative strategies. In this way, two different approaches have been proposed in the last years [2]: (i) the covalent attachment of the organocatalytic molecule to a side chain of the IL (commonly to the cationic part) to produce Functional Ionic Liquids (FILs) [3], and (ii) the covalent immobilization of ILs or FILs on a solid support in which the ionic liquid layer works as the catalyst solvent [4,5]. These procedures have provided stable catalysts. However, the high cost arisen from catalyst preparation what involves several reaction steps as well as the production of toxic wastes might restrict their implementation. Moreover, concerns have risen over the potential toxicity as well as low biodegradability of the currently employed ILs [6]. In this sense, some bio-ionic liquids have already been prepared from renewable and non-toxic natural products [7].

Herein, a new proposal that combines different approaches based on the Principles of Green Chemistry is described [8]. Firstly, the catalytic activity in the Michael addition reaction of a Bio-IL denoted as [Chol][Pro] (choline–proline) what has been synthesized from choline hydroxide ([Chol][OH]) and proline amino acid (Pro) by following an economical and green route has been evaluated [7c,9]. Proline-based ionic liquids have been studied as catalysts in this type of addition reactions [10]. However, to the best of our knowledge, the work presented here is the first one showing the catalytic activity of [Chol][Pro] in the Michael reaction. Subsequently, [Chol][Pro] was supported on different porous carbon materials by simple physical adsorption in organic media. Then, the catalytic activity of the heterogeneous systems was also studied. Carbon materials offer several advantages as solid supports such as relatively low cost, availability, high mechanical strength, chemical stability, and a pore structure as well as an attractive surface chemistry which allows modifications to suit the ILs immobilization needs [11]. Therefore, the purpose of this work was to obtain, in a simple way, efficient and stable Bio-IL/carbon material catalysts. The influence of the textural and surface chemical properties of the carbon materials on the catalytic activity of the supported Bio-IL is also discussed.

The Michael addition reaction is widely used in organic synthesis for C–C bond forming [12]. In particular, the addition between ketones and nitroalkenes to obtain nitroalkanes which are buildings blocks for agricultural and pharmaceutical products is very useful [13]. Therefore, the coupling of cyclohexanone and β-nitrostyrene to produce 2-(2-nitro-1-phenylethyl)cyclohexanone (Fig. 1) was selected in this work as the reaction test to evaluate the catalytic activity. To avoid the use of volatile solvents and to reduce the environmental pollution, all of the Michael reactions were performed under solvent-free reaction conditions and at room temperature.

2. Experimental

2.1. Synthesis of [Chol][Pro] Bio-IL

[Chol][Pro] (choline–proline) was prepared following a route previously reported [7c]: an excess of DL-proline (Pro) amino acid

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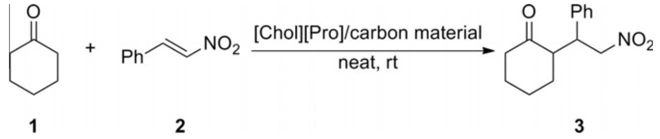

Fig. 1. Michael addition between cyclohexanone (**1**) and ß-nitrostyrene (**2**) to produce 2-(2-nitro-1-phenylethyl)cyclohexanone (**3**).

(73.2 mmol) was added to an aqueous solution of choline hydroxide ([Chol][OH]) 46 wt.% (61 mmol) and the mixture was stirred at room temperature for 24 h. Water was then removed under vacuum at 50 °C. After this step, acetonitrile (60 ml) and methanol (20 ml) were added to precipitate the unreacted amino acid. The mixture was stirred vigorously overnight, and then filtered through Celite. The solvents were evaporated under reduced pressure. Finally, the purified ionic liquid was dried under vacuum overnight at 60 °C and stored under moisture-free conditions until utilization. The ^{1}H NMR spectrum of [Chol][Pro] is provided as Supplementary material (Figure S1).

2.2. Carbon supports

Commercially available mesoporous (MB) and microporous (mB) carbon beads of particle size in the range 0.5–1.0 mm and a spherical shape were used as starting supports [14]. They are phenolic resin-based activated carbons. The mesoporous carbon MB was heated for 1 h at 1500 °C (MB-1500) and 2000 °C (MB-2000) in a graphite electrical furnace, at a heating rate of 10 °C min^{-1} in argon flow. The microporous mB was also treated at 1500 °C (mB-1500) under the same experimental conditions. Oxidation of MB (MB-LTA) was carried out in an Emitech K1050X reactor where oxygen was excited using RF energy (13.56 MHz) at a power of 75 W. The total sample exposure time was 30 min in successive treatments of 10 min each in order to attain a homogeneous carbon surface oxidation, the material being stirred manually between treatments.

2.3. Carbon supports characterization

The textural properties of the materials were measured by N_2 adsorption–desorption at −196 °C in a Micromeritics ASAP 2420 volumetric adsorption system. Before measurements, the samples were degassed overnight at 250 °C. The specific surface areas (S_{BET}) were calculated by applying the Brunauer–Emmett–Teller (BET) method, taking 16.2 nm^2 for the cross-sectional area of the nitrogen-adsorbed molecule. Total micropore volumes (VDR_{N2}) were assessed by applying the Dubinin–Radushkevich (DR) equation to the suitable adsorption data. Total pore volumes (V_t) were determined by the amount of N_2 adsorbed at $p/p^o = 0.99$. Pore size distributions were obtained by applying the DFT (Density Functional Theory) method to the N_2 adsorption isotherms and they are given as Supplementary material (Figure S2).

X-ray Photoelectron Spectroscopy (XPS) of carbon supports was performed on a SPECS Phoibos 100 analyser spectrometer using an Mg K_α X-rays (1486.6 eV) at a power of 120 W and in a residual vacuum of 10^{-7} Pa. Measurements were made with the analyser in fixed transmission mode and normal to the plane of the sample. An energy pass of 80 eV has been used to collect broad scan spectra (0–1100 eV). The total atomic percentage of oxygen present in the aprox. 10 nm of the upper layer and its distribution in different functional groups were calculated from the survey spectra by considering the integrated areas of the C1s peaks and their sensitivity factors. Corel level curve fitting was performed using a Shirley background and a standard least square algorithm. Each component was fitted to a convolution of a Gaussian and a Lorentzian functions (80:20).

2.4. Immobilization of [Chol][Pro] Bio-IL on the carbon supports

In a typical immobilization experiment, the Bio-IL (20 wt.%), dissolved in a minimal amount of anhydrous methanol, was mixed with the corresponding amount of support. Previously, the solid supports have been heated at 60 °C in a vacuum oven overnight to remove any residual moisture. To ensure an optimal penetration of the IL into the carbon material pores, the mixture was stirred at 275 rpm for 12 h followed by a careful removal of the solvent in a rotary evaporator. Then, the heterogeneous Bio-IL/carbon support system was dried at 40 °C in nitrogen flow and stored under moisture-free conditions.

2.5. General procedure for the Michael reaction

Michael addition reactions were carried out in a RR91034 12 place Carousel Reaction Station™ from Radleys Discovery Technologies. The carousel reaction tube was charged with the catalyst (20 mol%), the cyclohexanone (10 equiv., 0.5 ml) and the nitrostyrene (0.5 mmol), and the mixture was stirred at room temperature. The evolution of the reaction was followed by GC using a GC Agilent 6890N instrument.

3. Results and discussion

3.1. Catalytic activity of [Chol][Pro]

The Michael reaction conversions as well as the diasteroselectivity are given in Table 1. The *syn* isomer was the predominant product in all cases as identified by ^{1}H NMR [15]. A high yield (94%) of the Michael adduct was achieved after 24 h by using 10 equivalents of cyclohexanone in the presence of 20 mol% of [Chol][Pro]. Moreover, the diastereoselectivity was also reasonably high [9]. Conversion decreased to 86% by reducing cyclohexanone to two equivalents; however, similar diastereoselectivity was attained. When [Chol][Pro] catalyst concentration was also reduced (from 20 to 6 mol%), the reaction diastereoselectivity was noticeably improved but poor conversion was reached.

The catalytic activity of [Chol][Pro] was compared with that of proline what is commonly applied as catalyst in the Michael reaction [16]. As can be seen in Table 1, under similar conditions, [Chol][Pro] leads to a much higher conversion than Pro. However, the reaction diastereoselectivity was improved by using proline. Since almost all of the partial steps in the amine-catalyzed reactions are equilibriums, the high nucleophilicity of the proline will produce several equilibrium reactions with the electrophiles in the medium, thus leading to a low activity as it was previously observed for this catalyst [17]. On the contrary, the cholinate moiety of [Chol][Pro] seems to stabilize the development of the negative charge in the transition state of C–C bond formation, through

Table 1
Catalytic activity of [Chol][Pro] Bio-IL in the Michael addition between cyclohexanone and β-nitrostyrene.

Catalyst (mol%)	**1** (equiv.)	Time (h)	Conv. (%)	d.r. (*syn*:*anti*)
[Chol][Pro] (20)	10	24	94	80:20
[Chol][Pro] (20)	2	48	86	78:22
[Chol][Pro] (6)	2	48	40	89:11
Pro (20)	10	48	32	85:15

1, Cyclohexanone.