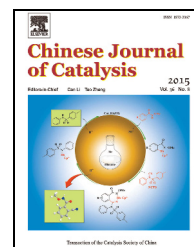


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## Article

# Synthesis, characterization, and application of silica supported ionic liquid as catalyst for reductive amination of cyclohexanone with formic acid and triethyl amine as hydrogen source



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## ABSTRACT

A silica supported ionic liquid was synthesized and characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy, X-ray diffraction, N<sub>2</sub> adsorption-desorption, and thermogravimetric analysis. All these techniques, especially SEM results indicated the presence of well-defined spherical particles having diameters larger than the pristine silica particles, confirming the successful immobilization of the ionic liquid. The prepared silica supported ionic liquid was used in the reductive amination of cyclohexanone under different conditions with different azeotropic mixtures of formic acid and triethyl amine as a hydrogen source. The catalyst showed efficient catalytic performance and excellent yields of *N*-cyclohexyl amine derivatives in the range of 58% to 84% at 30 °C. After completion of the reaction, the catalyst was easily recovered by simple filtration and reused for another five cycles without any significant impact on product yields. The obtained catalytic performance indicates that the present catalyst is green, very active, and reusable for the reductive amination of cyclohexanone.

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## 1. Introduction

Ionic liquids (ILs) have been considered as an efficient alternative to volatile organic compounds (VOCs) for “green processing” because of their nonvolatility, nonflammability, and high thermal stability [1–3]. Therefore, ILs have emerged as an active area of research for modern catalytic systems. The potential of ILs as catalysts for several chemical transformations has already been established. Moreover, ILs have been used as solvents in various biphasic IL-transition metal-catalyzed organic reactions to improve catalyst recycling and/or reusability [4–6]. In recent years, many researchers have given considerable attention to the immobilization of ILs, known as supported

ILs (SILs), using various organic [7,8] and inorganic supports [9,10] to improve the applicability of IL-based catalytic processes at an industrial level. Among the various forms of SIL systems, the supported ionic liquid phase (SILP) system is a very easy and effective catalyst system. In SILP systems, an ILfilm is immobilized on a high-surface area porous solid (e.g., silica) and the homogeneous catalyst can easily be dissolved in the IL layer [11,12]. The resulting solid combines the advantages of a heterogeneous catalyst with the active species being soluble in the IL phase and behaving as a homogeneous catalyst [13–16]. Furthermore, this SILP catalysis system incorporates the most attractive features of homogeneous catalysis, such as high activity and selectivity, with the useful quali-

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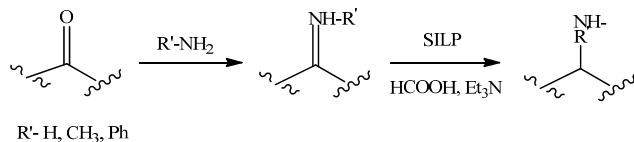
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ties of heterogeneous catalysts such as large surface area, easy product separation, high stability, and high reusability [17–19]. In this way, the SILP catalyst system reduces the differences between traditional homogeneous and heterogeneous catalysis systems. The search for efficient, convenient, and recyclable catalytic systems based on SILP to overcome the deficiencies in existing systems is one of the most fundamental but challenging problems in catalysis.

The wide range of applications for amines in the pharmaceutical and fine chemical industries has caused intense research into the development of efficient methods to produce these compounds in high yield and purity, considered important goals in organic synthesis [20–22]. One of the most widespread reaction types for this purpose, as well as for effective C–N bond forming, is the catalytic reductive amination of carbonyl compounds [23–25]. This approach involves two steps, the condensation of a ketone with a corresponding amine and subsequent imine hydrogenation using formic acid:triethyl amine as the H<sub>2</sub> donor (Scheme 1).

During past decades, the chemical modification of this reaction has evolved from the reductive amination of aldehyde and ketones. Previous reports on this reaction have focused on the use of transition metal catalysts [26–30], organocatalysts [31–35], and ILs [36] as the initiating species with reducing agents ranging from metal hydrides to H<sub>2</sub> gas [37–40]. The combination of formic acid and formaldehyde methylation of amines, known as the Eschweiler–Clarke reaction [41,42], is a method of wide synthetic use and has been the subject of critical investigation [43] in which a series of substituted benzylamines were used as model compounds. However, hydrogen donation from an azeotropic mixture of formic acid and triethyl amine was not exploited in these works [37–43]. To the best of our knowledge, the use of hydrogen donation from an azeotropic mixture of formic acid and triethyl amine for direct reductive amination reactions has not yet been explored. The atom economy and cleanliness of reductive amination makes it the most important catalytic method in synthetic organic chemistry. In an effort to develop a mild and efficient procedure for the reductive amination of carbonyl compounds, we have focused our attention towards the fabrication of an IL catalyst system. Imao et al. [44] first reported such a use of ILs, where 1-butyl-3-methyl imidazolium tetrafluoroborate [(BMIm)BF<sub>4</sub>] was used as the reaction medium for the direct reductive amination of carbonyl compounds with hydrogen catalyzed by an iridium complex.

In this study, we synthesized a SILP catalyst and applied it to a reductive amination reaction. The hydrogen donor source used here was an azeotropic mixture of formic acid and triethyl amine and the reaction was carried out at room temperature. In this way, the use of gaseous hydrogen and pressure reactors could be avoided, which rendered the reaction safer and easier



**Scheme 1.** Reductive amination of ketones.

to perform. Furthermore, we described a variety of possible modifications of this particular catalytic system, such as eco-friendly usage of ILs, immobilization on solid supports, and use of other simple chemicals as the hydrogen source.

## 2. Experimental

### 2.1. General

Methyl imidazole (99.0%), 1-chloroacetic acid (99.0%), cyclohexanone (99.0%), Na<sub>2</sub>CO<sub>3</sub> (99.0% IR grade), Na<sub>2</sub>SO<sub>4</sub> (99.0% IR grade) and all amine derivatives listed in Tables 2 and 4 were purchased from Sigma-Aldrich. All the solvents used in the reactions were purchased from commercial sources and distilled from the relevant agents prior to use. Ultrapure water (double distilled water purified with a Milli-Q system) was used to prepare aqueous solutions. Suitable absorptive capacity, flow ability, low cost, high stability, and high reusability are important considerations for catalyst supports used in heterogeneous catalyst systems. Therefore, we selected amorphous silica as the supporting material for the immobilization of the prepared ILs.

### 2.2. Preparation

#### 2.2.1. Preparation of [Cmmim<sup>+</sup>][Cl<sup>-</sup>]

The IL 3-(carboxymethyl)-1-methyl-1H-imidazol-3-ium chloride ([Cmmim<sup>+</sup>][Cl<sup>-</sup>]) was synthesized according to a previously reported procedure [45]. In brief, monochloro acetic acid (6.73 g, 0.10 mol) and 1-methylimidazole (8.21 g, 0.10 mol) were added to a round-bottom flask containing 50 mL of acetonitrile and fitted with a reflux condenser. The resulting mixture was heated for 24 h at 80 °C with continuous stirring. After completion of the reaction, the excess solvents were evaporated under reduced pressure and the obtained product was washed with diethyl ether (30 mL) and dried under vacuum for 24 h, resulting in a slightly yellow colored liquid product (yield: 90%).

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, 25 °C): δ 3.92 (s, 3H), 5.07 (s, 2H), 7.49 (s, 1H), 7.50 (s, 1H), 8.77 (s, 1H); <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O, 25 °C): δ 47.2, 53.3, 126.4, 141.2, 172.9; FTIR: 3404, 3111, 3092, 2964, 2852, 1710, 1637, 1581, 1454, 1177, 1078, 758 cm<sup>-1</sup>.

#### 2.2.2. Preparation of [Cmmim<sup>+</sup>][Tf<sub>2</sub>N<sup>-</sup>]

A solution of 4 g of bis(trifluoromethane)sulfonamide lithium salt in 12 mL of acetonitrile and 2 g of [Cmmim<sup>+</sup>][Cl<sup>-</sup>] were mixed in a 50-mL round bottom flask to synthesize (carboxymethyl)-1-methyl-1H-imidazol-3-ium-bis((trifluoromethyl)sulfonyl)amide ([Cmmim<sup>+</sup>][Tf<sub>2</sub>N<sup>-</sup>]). After stirring for 1 h at room temperature, the resulting slightly yellow viscous liquid was filtered and dried in a vacuum oven for 24 h (yield: 85%).

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, 25 °C): δ 3.92 (s, 3H), 5.07 (s, 2H), 7.50 (s, 1H), 7.51 (s, 1H), 8.77 (s, 1H); <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O, 25 °C): δ 40.1, 47.2, 53.3, 61.8, 126.3, 126.4, 141.2, 172.9; FTIR: 3404, 3111, 3092, 2964, 2852, 1710, 1637, 1581, 1454, 1177, 1078, 971, 834.5, 758.4, 648.4 cm<sup>-1</sup>.

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