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A novel and efficient procedure for the preparation of benzyl alcohol by hydrolysis of benzyl chloride catalyzed by PEG_{1000}-DAIL[BF_4]/$Fe_2(SO_4)_3$ under homogeneous catalysis in aqueous media

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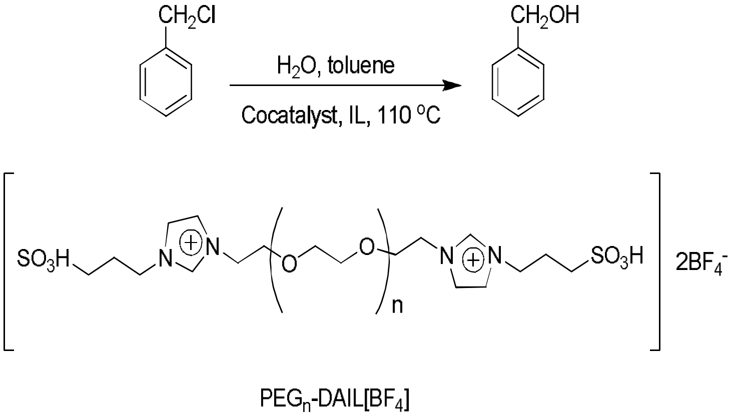
In this work, benzyl alcohol was obtained in 96% excellent yield by hydrolysis of benzyl chloride catalyzed by the recyclable temperature-dependant phase-separation system that comprised the ionic liquid PEG_{1000}-DAIL[BF_4], toluene and ferric sulfate under homogeneous catalysis in aqueous media. This novel method not only enhanced the yield, but also made the operating units easy workup. The catalytic system can be recycled or reused without any significant loss of catalytic activity. The mechanism of hydrolysis reaction and the process of catalysis in the thermoregulated ionic liquid bi-phase system were also proposed.

Keywords: Benzyl alcohol; Benzyl chloride; Hydrolysis; Thermoregulated ionic liquid biphasic system

1. INTRODUCTION

Benzyl alcohol is promising key intermediate in the synthesis of a variety of chemicals such as pharmaceuticals, dyes, flavors, perfume, food additive, etc [1-6]. Methods concerning the manufacture of benzyl alcohol have been well documented in previous papers [7-30], such as hydrolysis of benzyl chloride, oxidation of toluene, reduction of benzoic acid or benzaldehyde [7-14]. The most commonly employed procedures for prepare of benzyl alcohol have been the use of alkalines and the phase transfer catalysts as the promoted catalysts [15-21]. However the disadvantages of the alkaline hydrolysis are the additional use of base, the formation of dibenzyl ether and the production of aqueous waste liquors. There are also investigations into the hydrolysis in homogeneous mixtures of benzyl chloride, water, a water-soluble solubilizer (e.g. alcohol, acetic acid, dioxin, DMSO) and the metal salts (e.g. $HgCl_2$, $Hg(NO_3)_2$, Na_2WO_4, $CuSO_4$, CuCl) using as the catalysts [22-26]. Among these metal salts, copper and its salts are effective catalysts[26]. These catalyst systems, in general, suffer from the inherent problems of isolation of the hydrolysis products, difficulty of catalyst recovery, environmental hazards, toxicity, etc. Other notable methods to accomplish this include the use of microwave and elevated water [27-30]. Some of these procedures are invariably associated with one or more disadvantages such as high cost, high temperature, special apparatus, etc. Consequently, there is a great need to develop an efficient procedure for the synthesis of benzyl alcohol.

Ionic liquids (ILs), combining their interesting physical and chemical properties with a negligible vapor pressure, unique permittivity and excellent thermal stability, have recently been widely used for reaction media, separation solvents, and novel electrolytes [31-36]. However, these ILs are inevitably associated with one or more disadvantages such as low recovery ratio, high cost, etc. In view of both the advantages and disadvantages of homogeneous and heterogeneous catalysts, and to improve catalyst recovery, multiphase systems, such as phase-transfer catalysis [37], thermoregulated phase-transfer catalysis [38], and liquid–liquid biphasic catalysis [39], have been studied. Recently, some novel temperature-dependent ionic liquid biphasic catalytic systems have been reported [40-43], and because of their advantages such as high product yield and stability at high temperatures, reusability in the reaction, etc., they provide us a novel route for the separation of product from the reaction system and recycling of catalysts. The objectives of the present work are to report a novel and efficient procedure for synthesis of benzyl alcohol by hydrolysis of benzyl chloride catalyzed by PEG-1000-based dicationic acidic ionic liquid (PEG_{1000}-DAIL[BF_4]) in combination with ferric sulfate ($Fe_2(SO_4)_3$) and toluene in aqueous media (Scheme 1).



Scheme 1. Synthesis of benzyl alcohol catalyzed by PEG_{1000}-DAIL[BF_4]/$Fe_2(SO_4)_3$.

2. EXPERIMENTAL

2.1. Apparatus and Reagents

All the chemicals were from commercial sources without any pretreatment. All reagents were of analytical grade. The ionic liquids were synthesized according to the literature procedures [44]. High performance liquid chromatography (HPLC) experiments were performed on a liquid chromatograph (Dionex Softron GmbH, America), consisting of a pump (P680) and ultraviolet-visible light detector (UVD) system (170U). Elemental analysis were performed on a Vario EL III instrument (Elmentar Analysen Systeme GmbH, Germany).

2.2 Preparation of benzyl alcohol

A mixture of benzyl chloride (1.26 g, 10 mmol), toluene(10mL),water (10 mL, 0.5 mol), $Fe_2(SO_4)_3$ (1.0 g, 2.5 mmol), and PEG_{1000}-DAIL[BF_4] (10 mL, 9mmol) were added in a 100 mL round flask equipped with reflux condenser and oil-bath. The reaction mixture was stirred for 40 min at 110 °C, the reaction progress was monitored by HPLC. Upon completion, the mixture was cooled to room temperature. The organic phase was separated by decantation and dried with anhydrous sodium sulfate. Then the crude mixture was purified by column chromatography on silica gel to afford a colorless oil of benzyl alcohol (1.03 g, 96% yield). The next run was performed under identical reaction conditions.

3. RESULTS AND DISCUSSION

In a preliminary study, the hydrolysis of benzyl chloride was carried out in oil–water biphasic system in the presence and absence of PEG_{1000}-DAIL[BF_4] at 110 °C. As shown in Figure 1, in the absence of PEG_{1000}-DAIL[BF_4], the hydrolysis reaction proceeded very slowly, and only 24% yield was obtained after 1 h. The results mean that $Fe_2(SO_4)_3$ alone does not work as an effective catalyst in the hydrolysis reaction. Reaction performed with PEG_{1000}-DAIL[BF_4] proceeded very rapidly and the yield reached 96% in 1 h, which demonstrated the high catalysis efficiency of PEG_{1000}-DAIL[BF_4].

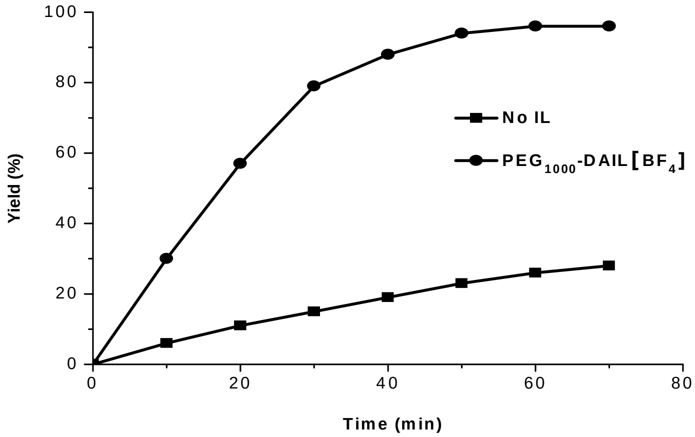


Fig. 1. Plot of the hydrolysis degree vs. time in presence and in absence of PEG_{1000}-DAIL[BF_4].

The effects of different ionic liquids such as PEG_{600}-DAIL, PEG_{800}-DAIL, PEG_{1000}-DAIL, PEG_{1000}-DAIL[BF_4], PEG_{1000}-DAIL[PF_6], and PEG_{1000}-DAIL[OTf] were shown in Figure 2, and it was observed that PEG_{1000}-DAIL[BF_4] demonstrated the best performance. The different catalytic abilities of the ILs (PEG_{600}-DAIL, PEG_{800}-DAIL, and PEG_{1000}-DAIL) should be attributed to their different abilities of forming homogeneous catalysis mediums by exhibiting a temperature-dependent phase behavior with toluene (i.e. the thermoregulated biphasic behavior of mono-phase under high temperature and bi-phase under room temperature). Under the same conditions, the IL who form homogeneous catalysis medium in combination with toluene more easily will lead to a larger increase in the effective reactant concentration, which increases the encounter probability between the reactive species. Thus, the observed rate and yield of the reaction is PEG_{1000}-DAIL> PEG_{800}-DAIL> PEG_{600}-DAIL.

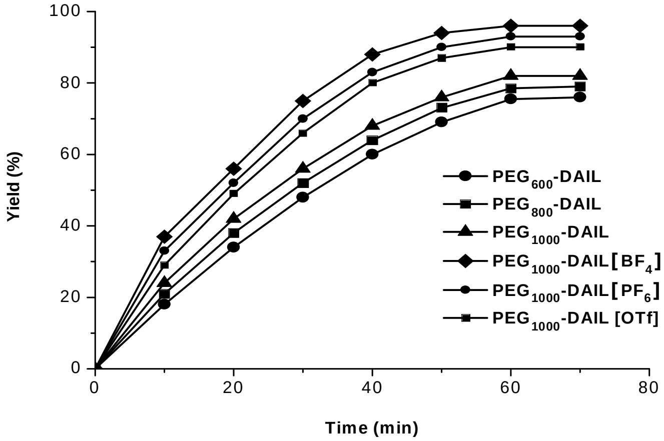


Fig. 2. Influences of different types of ILs on the hydrolysis.

As shown in Figure 3, it was observed that a lower yield of the product was obtained while the same reaction condition was carried out in the absence of a cocatalyst. The result indicates that the cocatalyst must play an important role in accelerating the rate of the reaction to some extent. In this reaction, we tried to use some types of cocatalysts in the reaction, the results showed that $Fe_2(SO_4)_3$, $CuSO_4$ and $Cu(OAc)_2$ were almost the same effective cocatalysts. Among them, $Fe_2(SO_4)_3$ was found to be the most effective cocatalyst in terms of yield and reaction rate.

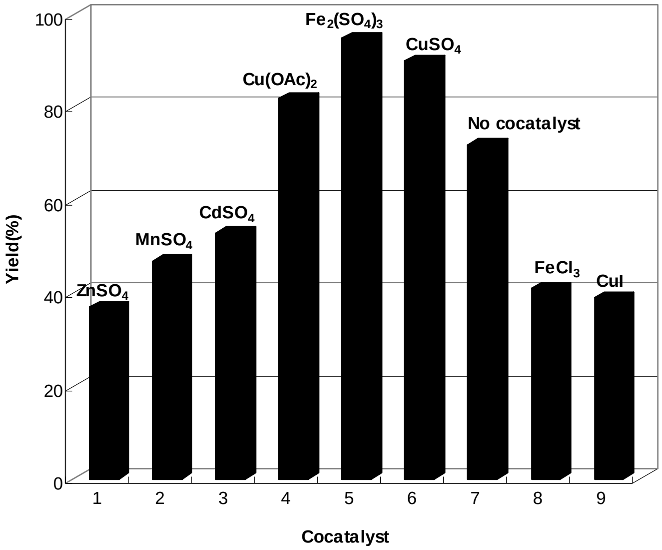


Fig. 3. Influences of different types of cocatalysts on the hydrolysis.

The influences of the amount of concentrated PEG_{1000}-DAIL[BF_4] at 110 °C are shown in Figure 4. In the absence of IL, the hydrolysis reaction proceeded slowly, the yield of benzyl alcohol was increased with the increase in PEG_{1000}-DAIL[BF_4] amount. The yield reached maximum at 1.0 of the volume ratio (IL / water = 1). However, further addition of the IL, under the same conditions, did not enhance significantly the yield.

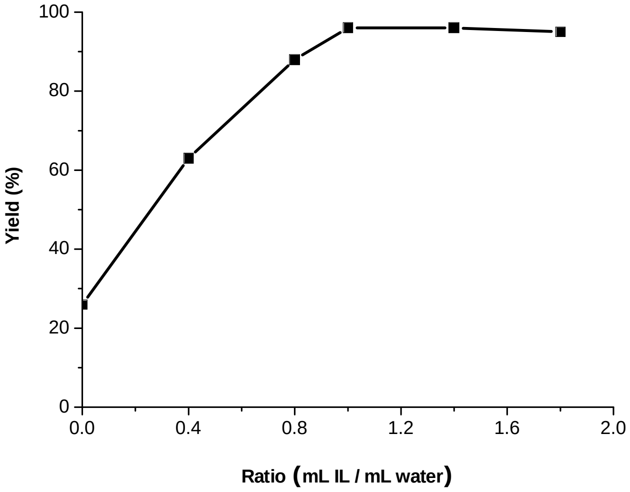


Fig. 4. Influences of the amount of PEG_{1000}-DAIL[BF_4] on the hydrolysis.

Figure 5 shows the influences of reaction temperature on the hydrolysis. The catalytic activities increased with the increase in reaction temperature, and the yield reached maximum at 110 °C. However, further increase in the temperature, the yield decreased slowly. This is due to the formation of dibenzyl ether at higher temperatures which were observed in LC chromatogram. These results show that the moderate temperature, such as 110 °C enhanced the reaction.

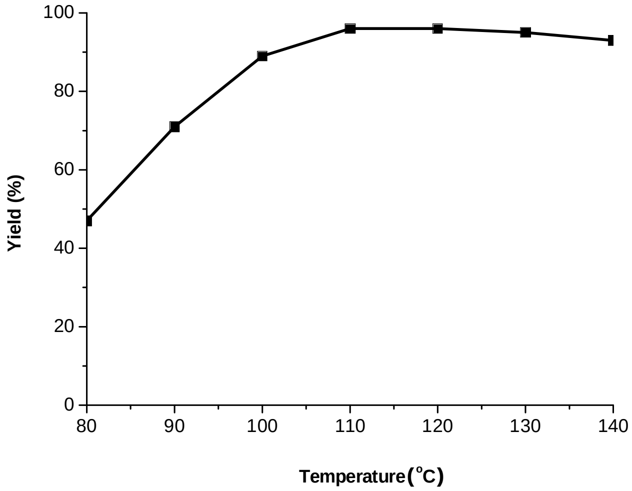


Fig. 5. Influences of reaction temperature on the hydrolysis.

In addition, the catalytic system could be typically recovered and reused for subsequent reactions with no appreciable decrease in yields and reaction rates (Figure 6). The recycling process involved the removal of the top oil layer (toluene containing product) by decantation. The bottom aqueous layer (catalytic system) was concentrated under vacuum to remove the water and hydrogen chloride (the hydrolysis product). Fresh substrates and toluene were then recharged to the residual PEG_{1000}-DAIL[BF_4]/$Fe_2(SO_4)_3$ and the mixture was heated to react once again. The procedure was repeated 8 times in the hydrolysis of benzyl chloride, and only 5.6% loss of weight was observed.

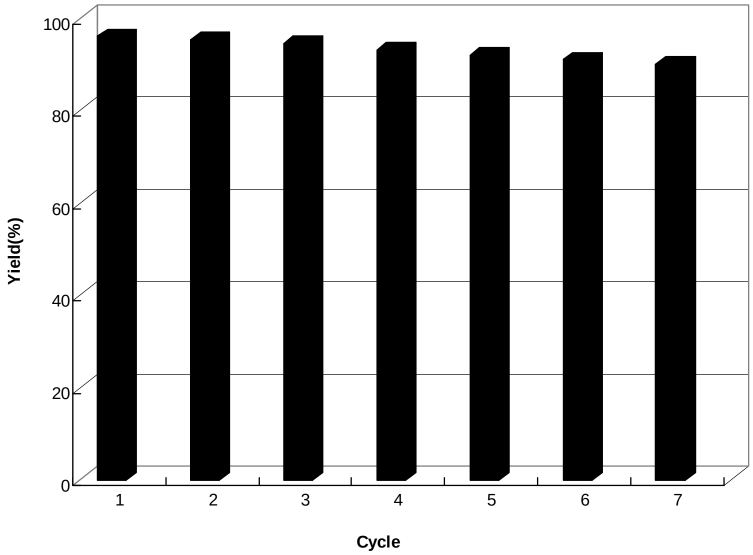
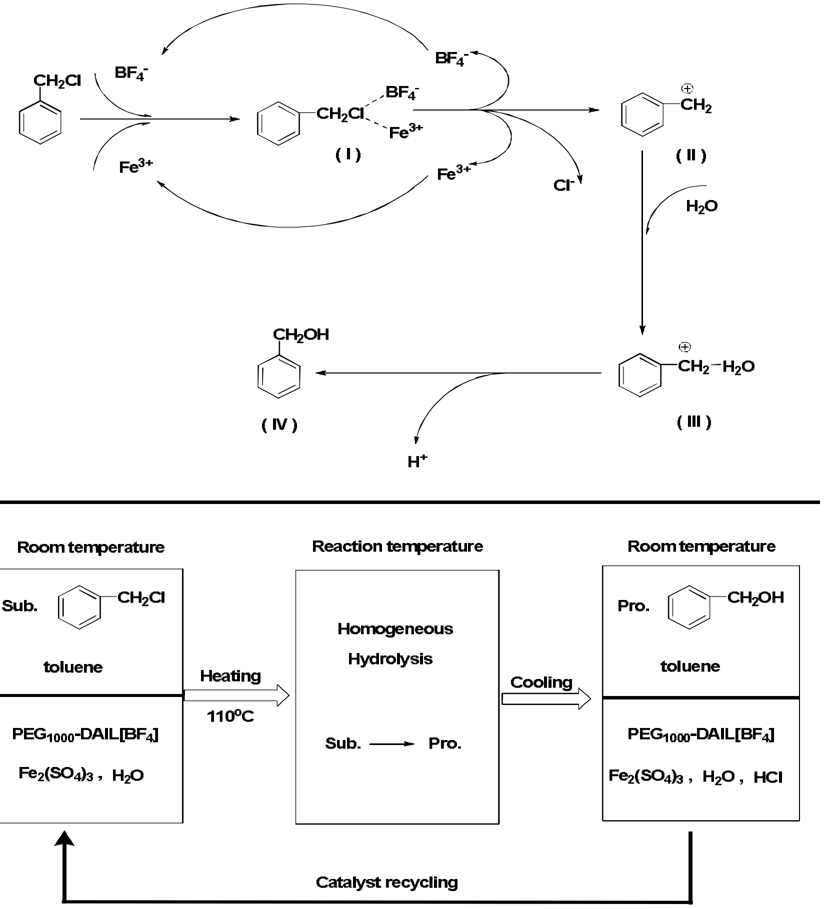


Fig. 6. Repeating reactions using recovered PEG_{1000}-DAIL[BF_4].

The excellent catalytic abilities of PEG_{1000}-DAIL[BF_4]/$Fe_2(SO_4)_3$ suggest that the hydrolysis reaction among benzyl chloride, water, toluene, ferric sulfate and PEG_{1000}-DAIL[BF_4] has a particular mechanism. Scheme 2 shows a possible mechanistic pathway for the synthesis of benzyl alcohol. Before the hydrolysis, there exists an obvious oil–water biphasic system: the under layer (water phase) consists of PEG_{1000}-DAIL[BF_4], $Fe_2(SO_4)_3$, and water, PEG_{1000}-DAIL[BF_4] is dissolved completely in the aqueous medium; the upper layer (oil phase) consists of benzyl chloride and toluene. During the process of hydrolysis, the oil–water biphasic system disappears and a homogeneous reaction medium is formed. In this case, it is considered that the stable benzyl cation is formed during the hydrolysis process [21-23]. Firstly, benzyl chloride reacts with the Fe^{3+} and BF_4^- to form transition state (**I**) and then, **I** eliminates the chlorine ion (Cl^-) to yield the stable benzyl cation (**II**), then **II** is attacked by the nucleophile (H_2O) yielding the transition state(**III**), finally **III** eliminates the proton (H^+) to yield the desired product benzyl alcohol (**IV**). After the completion of the reaction, a complete phase-separation is formed again after cooling to room temperature, the upper layer of toluene containing product was removed by decantation, and the under layer of the catalytic system, containing PEG_{1000}-DAIL[BF_4]/$Fe_2(SO_4)_3$ and hydrochloric acid was concentrated to remove generated water through water knockout drum and then recycle. The PEG_{1000}-DAIL[BF_4] plays a very important role in the hydrolysis process to locally concentrate the reacting species near them by exhibiting a temperature-dependent phase behavior with toluene (i.e. the thermoregulatedm biphasic behavior of mono-phase under high temperature and biphase under room temperature), which leads to a large increase in the effective reactant concentration and the excellent yield of benzyl alcohol is obtained accordingly.



Scheme 2. Possible mechanism for the hydrolysis of benzyl chloride.

4. CONCLUSION

In conclusion, we have developed a novel and efficient synthetic pathway for the preparation of benzyl alcohol by hydrolysis of benzyl chloride catalyzed by PEG_{1000}-DAIL[BF_4]/$Fe_2(SO_4)_3$ in aqueous media in a 96% excellent yield. Compared to the synthetic methods reported in previous literatures [7-30], the novel method not only enhanced the yield, but also made the operating units easy workup. Simple reaction conditions, good thermoregulated biphasic behavior of IL and facile manipulations in the isolation of the product are the attractive features of this methodology. Moreover, the excellent recyclability of the catalytic system makes this procedure cleaner, which is a good example of green chemistry technology.

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