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The first non-acid catalytic synthesis of *tert*-butyl ether from *tert*-butyl alcohol using ionic liquid as dehydrator†

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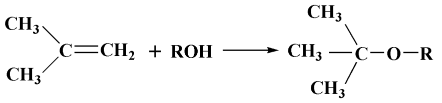
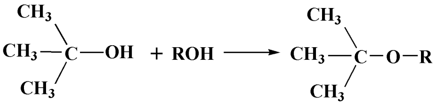
Methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), and isopropyl *tert*-butyl ether (IPTBE) have been synthesized for the first time over a non-acid ionic liquid as catalyst and dehydrator with high conversion (> 90%) and selectivity (> 90%) under mild conditions.

As it is known, asymmetrical tertiary alkyl ethers, especially methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE) and isopropyl *tert*-butyl ether (IPTBE), are particularly useful as octane improvers for gasoline due to the rapidly increasing demand for lead-free octane boosters for gasoline[1,2]. MTBE, ETBE or IPTBE are currently synthesized by reacting isobutylene with corresponding alcohols (synthesis route **1**) and are industriously manufactured over Amberlyst-15[3] with satisfactory conversion and selectivity although several limitations such as thermal instability and loss of acid sites were difficult to overcome. At the same time, large amounts of work on zeolites or zeolite supported catalysts[4–6] were also conducted but all studies mentioned above could not satisfy the enormous increase of the demand of oxygenates in the coming years because of the growing problem of the availability of isobutene as a raw material.[7] Therefore, to develop a process without requiring isobutene as a building block would be advantageous and an efficient process involving the reactions between methanol or ethanol and *tert*-butyl alcohol (TBA) to afford asymmetrical tertiary alkyl ethers is highly desirable because TBA (synthesis route **2**) is readily available commercially through isobutane oxidation.[7,8]



$$\mathrm{(CH_3)_2C{=}CH_2 + ROH \longrightarrow (CH_3)_3C{-}O{-}R} \qquad (1)$$



$$\mathrm{(CH_3)_3C{-}OH + ROH \longrightarrow (CH_3)_3C{-}O{-}R} \qquad (2)$$

In the previously reported papers, the catalysts selected for the etherization of TBA were various solid acids including heteropoly acid, titania supported phosphoric acid, acidic montmorillonite clay and zeolite modified by fluorosulfonic acid or fluorophosphoric acid, *etc*, but their catalytic performance could still not satisfy the requirement of industrial application at this stage.[9–12] The major problems associated with these processes were the formation of large amount of isobutene with an increase of TBA conversion because acids were also effective catalysts for dehydration of TBA to yield isobutene. Therefore, how to design and synthesize a catalytic system that may avoid the dehydration of TBA has long been pursued.

In this communication, it was found that an ionic liquid[13,14] could be an effective dehydration agent for the etherization reaction with a high yield if an appropriate ionic liquid was used, especially if non-acid[15,16] ionic liquids with BF_4^- anion, was selected.

Following ionic liquids were used in this reaction: $emimBF_4$ (1-ethyl-3-methyl-imidazole), $bmimBF_4$ (bmim = 1-butyl-3-methyl imidazolium), $dmimBF_4$ (1-decyl-3-methyl imidazolium), $cmimBF_4$ (1-cetyl-3-methyl imidazolium), bmimCl, $bmimPF_6$ and $BPyBF_4$ (BPy = 1-butyl pyridinium). All ionic liquids were synthesized according to previous papers[17,18] with small modifications and evaporated with a vacuum pump at 120 °C (5 mmHg) before use. All reactions were conducted in a 90 ml autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, 3 ml ionic liquid, 3 ml TBA and 6 ml methanol (ethanol or isopropanol) were successively introduced into the reactor without any additional organic solvent and cocatalyst. Then the reaction proceeded at 130 °C for 3 h. After reaction, a mixture of desired products, unreacted substrates and byproducts (in some cases) could be separated from the ionic liquids containing some water by simple distillation. The ionic liquid was evaporated with vacuum pump at 120 °C (5 mmHg) for 30 min to remove water and reused next time. Qualitative analyses were conducted with a HP 6890/5973 GC-MS with chemstation containing a NIST Mass Spectral Database. Quantitative analyses were conducted with a HP 1790 GC equipped with a FID detector.

All results of the etherization of TBA are listed in Table 1. As shown, the effect of the substituted alkyl chain of the imidazolium cations on the reaction was investigated first. Only 19% and 39% of conversions were achieved in $emimBF_4$ and $bmimBF_4$ ionic liquids while even no byproduct was detected (entries 1, 2). The best result was obtained when using $dmimBF_4$ as dehydrator and catalyst with a conversion of 93% and a selectivity of 97% (entry 3). Nearly 100% of conversion was obtained when the reaction was conducted at 175 °C while the selectivity was only 80% because *ca.* 20% of TBA was converted into isobutene (entry 4). Furthermore, some dimethyl ether (about 10% based on the methanol) was also detected under such reaction conditions, which indicated that the ionic liquid exhibit higher catalytic activity at higher reaction temperature and the dimethyl ether might be effectively synthesized if appropriate reaction conditions were selected. At

Table 1 Etherization results of *tert*-butyl alcohol in different ionic liquids[a]

Entry	Ionic liquid	Alcohol	Conversions (%)	Selectivities (%)
1	$emimBF_4$	MeOH	19	~ 100
2	$bmimBF_4$	MeOH	39	~ 100
3	$dmimBF_4$	MeOH	93	97
4[b]	$dmimBF_4$	MeOH	~ 100	80
5	$cmimBF_4$	MeOH	45	~ 100
6[c]	$dmimBF_4$	MeOH	94	96
7	bmimCl	MeOH	~ 0	—
8	$bmimPF_6$	MeOH	~ 0	—
9	$BPyBF_4$	MeOH	~ 0	—
10	$dmimBF_4$	EtOH	95	94
11	$dmimBF_4$	i-PrOH	91	98

[a] The byproduct was only isobutene. [b] The reaction was conducted at 175 °C. [c] The ionic liquid was used for the third time.

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the same time, the conversion decreased to 45% while no isobutene formed if cmimBF_4 was used as catalyst (entry 5).

All the results mentioned above show that an imidazolium cation with a substituted alkyl chain of about ten carbons was the best catalyst for this etherization reaction. The experiment results also showed that no longer equilibrium time for the reaction achieving high conversion was needed and no catalyst deactivation was observed when the ionic liquid was reused several times because similar conversion and selectivity were obtained in comparison with that of the ionic liquid used for the first time (entry 6), this result was much better than that reported previously.[11]

Surprisingly, no reaction occurred when ionic liquids bmimCl, bmimPF_6 and BPyBF_4 were used as catalysts (entries 7–9). This showed that both the anions and cations of the ionic liquids had a strong impact on the catalytic activity. Good results were also obtained when dmimBF_4 catalyst was further used in the synthesis of other two important *tert*-butyl ethers, *i.e.* ETBE and IPTBE (entries 10, 11), which conversions were 95% and 91% with more than 90% of selectivities.

As to the reaction mechanism of this process, it is not clear at this stage. The understanding of the mechanism of catalysis in ionic liquids is still in its infancy. The experimental results showed that poor results were obtained over the ionic liquids either with stronger acidic BMImPF_6 or with stronger basic bmimCl in comparison with the excellent catalytic performance given by non-acid or neutral dmimBF_4. The ionic liquids are composed only of ions, such ionic nature can affect the course of the reactions. It can be conjectured that the strong electrostatic field possessed by the dialkyl imidazolium ionic liquids mediated with length of side alkyl chain substituents, may play an important role in initiating the desired reaction and a traditional acid or base catalytic mechanism was not involved in this process.

In summary, this, to the best of knowledge, is the first report of a non-acid and highly effective ionic liquid catalyst system for synthesis of *tert*-butyl ether, and it was also the first time to show that an ionic liquid could also be an effective dehydration agent. Further investigation about the reaction mechanism is now on-going.

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