The tetramethylguanidine-based ionic liquid-catalyzed synthesis of propylene glycol methyl ether†

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Tetramethylguanidine-based ionic liquids were used as effective catalysts for the synthesis of propylene glycol methyl ether from methanol and propylene oxide. 1-Methoxy-2-propanol was produced in nearly 90% yield under much milder conditions. The catalyst can be reused at least ten times without any considerable decrease in its activity and selectivity.

Ionic liquids (ILs), which are organic salts with a melting point below 100 °C, have attracted much attention in recent years. Compared with traditional organic solvents, ILs have a negligible vapor pressure, high thermal stability, non-flammability and reusability.[1–3] They have been investigated extensively in organic synthesis as solvents or catalysts.[1,3–10] As both the anionic and the cationic part of ILs can be easily varied, their properties can be tuned for specific purposes. In recent years, a great number of functional ILs have been synthesized for different purposes.[11] In previous work, we reported the preparation and application of 1,1,3,3-tetramethylguanidine (TMG)-based ILs.[12] They have been applied in carrying out Henry[13] and direct aldol reactions,[14] preparing immobilized catalysts,[15,16] and absorbing SO_2 from simulated flue gases.[17]

Propylene glycol methyl ether (PGME) is a kind of fine chemical that is widely used as an "alkahest" due to its ether bond and hydroxyl group, which is hydrophobic and hydrophilic, respectively. It is expected to be a safe substitute for toxic ethylene glycol ether because of the negligible toxicity of propylene glycol ether.[18] PGME is generally prepared from the addition of methanol to propylene oxide (PO) catalyzed by acids or bases.[19] As shown in Scheme 1, the product obtained by basic catalysts is different from that produced by acidic catalysts due to the different mechanisms involved. The ring of PO might preferentially open at the least sterically hindered position over a basic catalyst, leading to the predominant production of the secondary alcohol 1-methoxy-2-propanol. However, acidic catalysts provide a mixture of secondary and primary alcohols; the proportion of the two products depends on the acid strength.

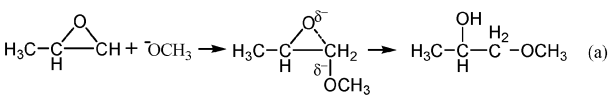
Compared to secondary alcohols, primary alcohols (such as 2-methoxy-1-propanol) have a much higher toxicity. Therefore, high selectivity for the secondary alcohol is preferred for this process and the utilization of basic catalysts has attracted much attention. In past decades, many homogenous base catalysts (NaOH, NaOR, NR_3) were exploited and showed high selectivity for secondary alcohols, but they had drawbacks in separation, liquid waste treatment and corrosion. In order to overcome these problems of liquid catalysts, solid bases, such as anionic double hydroxide clays,[20] basic zeolites[21] and basic metal oxides,[22–24] have been used to catalyze the synthesis of propylene glycol ether. The reaction temperature is usually from 393 to 433 K for these catalysts.

Catalysts with a high activity under mild temperatures are always attractive for most chemical reactions. In this work, task-specific TMG-based ILs were applied to catalyze the synthesis of PGME from methanol and PO. ILs could overcome all the above-mentioned drawbacks, possessed a high activity and could be recovered easily. The selectivity for 1-methoxy-2-propanol was about 95% and the yield of the two isomers was nearly 90% at 343 K, which is much lower than the temperatures of the reactions accelerated by other catalysts (393–433 K). The TMG-based IL can be recovered and used at least ten times without considerable reduction in its activity and selectivity.

Table 1 lists the yield of PGME and the selectivity for 1-methoxy-2-propanol in the reaction of methanol (MeOH) and PO promoted by different catalysts. TMG is a strong base and shows a good catalytic activity; however, the separation of TMG and the products after the reaction is difficult. The TMG-based ILs also show high activities in the reaction of PO and MeOH. Under the same reaction conditions, the catalytic activity sequence was [TMG][Ac] > [TMG][Lac] > [TMG][Tfa], which is consistent with that seen in the catalysis of the direct aldol reaction.[11]

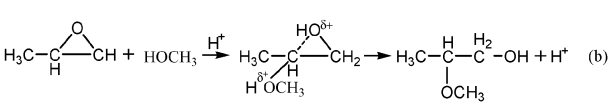
Fig. 1 shows the yield of PGME and the selectivity for 1-methoxy-2-propanol at different temperatures with [TMG][Ac] as the catalyst. As the temperature was increased from 323 to 343 K, the yield of PGME increased from 27.6 to 87.6%.

Base-catalyzed reaction



(a)

Acid-catalyzed reaction



(b)

Scheme 1 The reaction of propylene oxide and methanol using different catalysts

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Table 1 Comparison of the yield and selectivity in the reaction catalyzed by different ILs[a]

Catalyst	Yield (%)	Selectivity (%)
TMG	84.5	94.9
[TMG][Ac]	87.6	94.7
[TMG][Lac]	78.3	95.0
[TMG][Tfa]	4.2	93.3

[a] Reaction conditions: PO, 20 mmol; MeOH, 60 mmol; catalyst, 0.5 mmol; reaction temperature, 343 K; reaction time, 3 h.

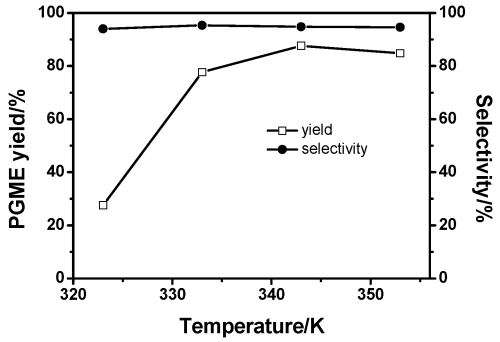


Fig. 1 The effect of reaction temperature on the reaction. Reaction conditions: PO, 20 mmol; MeOH, 60 mmol; [TMG][Ac], 0.5 mmol; reaction time, 3 h.

The yield decreased slightly when the temperature was increased to 353 K. The selectivity did not change as the temperature was increased. As a whole, the selectivity was not sensitive to temperature. Based on these preliminary results, we conducted further experiments at 343 K.

The effect of the reaction time on the reaction was investigated at 343 K; the results are given in Fig. 2. The yield increased from 19.1 to 87.6% as the reaction time was increased from 1 to 3 h. The yield was almost unchanged upon further extending the reaction time. In addition, the effect of the reaction time on the isomer selectivity was not considerable. These data demonstrate that a satisfactory yield and selectivity could be obtained with a reaction time of 3 h.

Fig. 3 shows the influence of the MeOH/PO molar ratio on the yield of PGME and the selectivity for 1-methoxy-2-propanol at 343 K after 3 h. When the molar ratio was

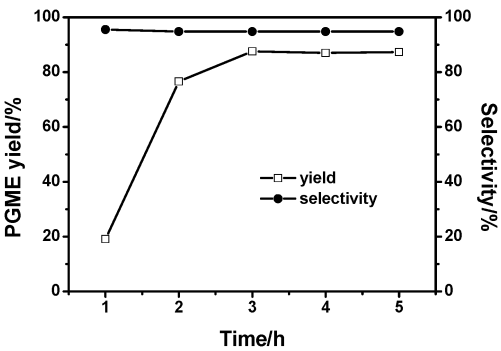


Fig. 2 The effect of reaction time on the reaction. Reaction conditions: PO, 20 mmol; methanol, 60 mmol; [TMG][Ac], 0.5 mmol; reaction temperature, 343 K.

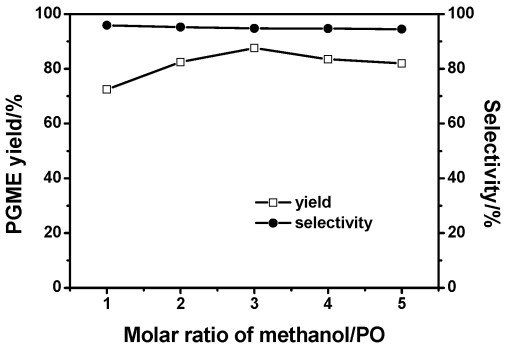


Fig. 3 The effect of the reactant ratio on the reaction. Reaction conditions: PO, 20 mmol; [TMG][Ac], 0.5 mmol; reaction temperature, 343 K; reaction time, 3 h.

changed from 1 to 3, PO could completely react with the MeOH, and the yield of PGME increased from 72.5 to 87.6%. When the MeOH/PO molar ratio was further increased to 5, the yield decreased to 82%. The selectivity decreased slightly with increasing molar ratio. Therefore, the optimal MeOH/PO molar ratio was about 3.

The reusability of [TMG][Ac] was tested in the synthesis of PGME. After each run, the product and excess MeOH were evaporated at 353 K. The IL was then dried in a vacuum at 333 K for 5 h and reused. The results of the reaction are shown in Fig. 4. The selectivity was almost unchanged after the catalyst had been reused 9 times. The yield decreased only slightly, indicating that the IL was reusable.

We also studied the catalytic performance of [TMG][Ac] for the reactions of methanol with styrene oxide and 1,2-epoxyhexane, respectively, and the results are presented Table S1.† It can be from the data in this table that a high yield could also be reached, but that a higher temperature and a longer time were required to complete the reaction.

In conclusion, the catalytic performance of TMG-based ILs for the reaction to synthesize PGME from methanol and PO has been studied. [TMG][Ac] has a higher catalytic activity than [TMG][Lac] and [TMG][Tfa]. It is very active, even at 343 K, and a high yield of PGME with a selectivity for the less

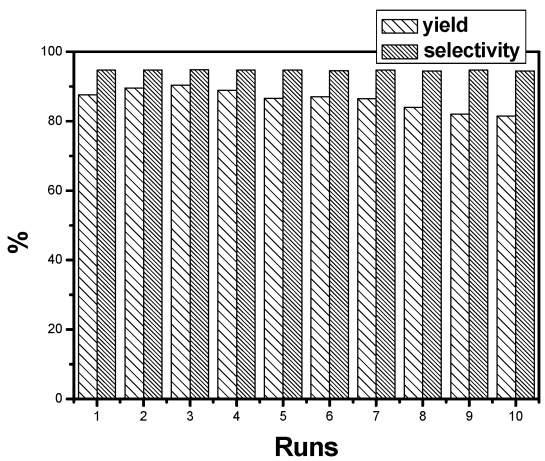
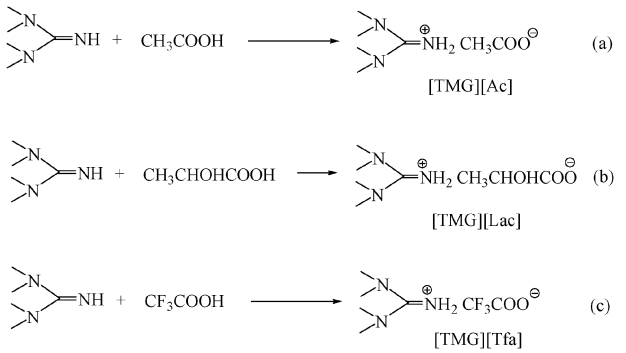


Fig. 4 A test of the reusability of the IL [TMG][Ac]. Reaction conditions: PO, 20 mmol; methanol, 60 mmol; [TMG][Ac], 0.5 mmol; reaction temperature, 343 K; reaction time, 3 h.



Scheme 2 The synthesis of the 1,1,3,3-tetramethylguanidine-based ILs.

toxic isomer 1-methoxy-2-propanol can be obtained. Moreover, after the reaction, [TMG][Ac] can be easily recovered and recycled without any considerably decrease in the yield or selectivity. This protocol provides a green and effective alternative for the synthesis of PGME at low temperature.

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Experimental

1,1,3,3-Tetramethylguanidine was purchased from the Baigui Chemical Company (Shijiazhuang, China). All acids and solvents (analytical grade) were purchased from the Beijing Chemical Reagent Plant (Beijing, China).

We have only described the procedure to synthesize 1,1,3,3-tetramethylguanidinium acetate ([TMG][Ac]) because those to prepare 1,1,3,3-tetramethylguanidium lactate ([TMG][Lac]) and 1,1,3,3-tetramethylguanidium trifluoroacetate ([TMG][Tfa]) are similar. The main difference is that the corresponding acids are used (Scheme 2). In a typical experiment, 100 mL of ethanol and 2.30 g of TMG (20.0 mmol) were loaded into a 250 mL flask in a water bath at 0 °C. Then, 20.0 mmol of CH_3COOH in 35 mL of ethanol was slowly charged into the flask with stirring. The reaction lasted for 2 h. The reaction mixture was evaporated under reduced pressure at 333 K. The crude oily residue was dissolved in 100 mL of ethanol, treated with active carbon, filtered and evaporated under vacuum.

The catalytic performance of the ILs was evaluated in a 6.5 mL batch reactor with a molar ratio of methanol to PO from 1 : 1 to 5 : 1. After running at the desired temperature for a suitable time under magnetic stirring, the reactor was cooled to room temperature. The products were analyzed by a GC (Agilent 6820) equipped with an FID detector and a capillary column (SUPELCOWAX 10, 30 m in length, 0.25 mm in diameter). *n*-Propanol was used as the internal standard to calculate the amount of the products. The yield of PGME (primary and second alcohols) is defined as the ratio of the number of moles of PGME produced in the reaction to the total number of moles of PO initially added. The selectivity for 1-methoxy-2-propanol is defined as the ratio of the number of moles of 1-methoxy-2-propanol to the number of moles of the two isomers.

$$\text{Yield} = \frac{\text{moles of (1-methoxy-2-propanol + 2-methoxy-1-propanol) produced}}{\text{moles of propylene oxide initially added}}$$

$$\text{Selectivity} = \frac{\text{mol(1-methoxy-2-propanol)}}{\text{mol(1-methoxy-2-propanol) + mol(2-methoxy-1-propanol)}}$$

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