Catal Lett (2010) 140:49–54
DOI 10.1007/s10562-010-0426-9

Immobilized 1,1,3,3-Tetramethylguanidine Ionic Liquids as the Catalyst for Synthesizing Propylene Glycol Methyl Ether

**Shuguang Liang · Yinxi Zhou · Huizhen Liu ·
Tao Jiang · Buxing Han**

Received: 21 June 2010 / Accepted: 30 July 2010 / Published online: 17 August 2010

Abstract In this work, we immobilized ionic liquid 1,1,3,3-tetramethylguanidium lactate on two solid supports, bentonite and SBA-15, by different methods. The prepared materials were used to catalyze the reaction of propylene oxide and methanol to produce propylene glycol methyl ether. 1-Methoxy-2-propanol was the predominant product. The influence of the amount of the catalyst, molar ratio of the reactants, reaction temperature and time on the yield and selectivity was studied. The two catalysts were proved to be efficient and reusable catalysts for the reaction.

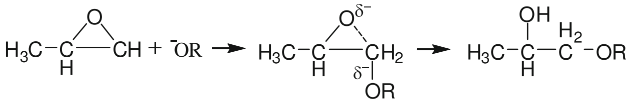
Keywords Propylene glycol methyl ether (PGME) · Ionic liquids · Propylene oxide (PO) · SBA-15 · Tetramethylguanidine · Methanol · Bentonite

1 Introduction

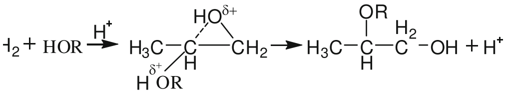
Ionic liquids (ILs) are organic salts that possess many different properties compared with traditional organic solvents, such as nonflammability, negligible vapor pressure, reusability, and high thermal stability [1–3]. They have been investigated extensively in organic synthesis as solvents or catalysts [1, 3–7]. As both the anionic and the cationic part of ILs can be easily varied, the properties of these compounds can be adjusted for specific purposes. In recent years, a great number of task-specific ILs was synthesized and applied [8, 9]. We previously reported the preparation and characterization of 1, 1, 3, 3-tetramethylguanidium (TMG)-based ILs [9]. They have been successfully applied to catalyze Henry [10] and direct aldol reaction [11, 12], immobilize metals to prepare catalysts [13, 14] and absorb SO_2 from simulated flue gases [15]. These uses are based on the electron lone pair of the guanidine cation. But there are very few work about the immobilized TMG-based ILs used as catalysts. Zhang et al. [16] reported that silica-supported hexaakylguanidinium chloride was the effective and recyclable catalysts for CO_2 fixation to produce cyclic carbonates.

Propylene glycol methyl ether (PGME) is one kind of fine chemicals widely used as solvent because of the ether bond and hydroxyl group, which is hydrophobic and hydrophilic, respectively. It is expected as a safe substitute for toxic ethylene glycol ether because of the negligible toxicity of propylene glycol ether [17]. PGME is conventionally derived from addition of methanol to propylene oxide (PO) catalyzed by an acid or a base. Generally, the mechanism was considered as follows [18, 19].

Basic catalysis



Acidic catalysis



S. Liang · Y. Zhou · H. Liu · T. Jiang (✉) · B. Han (✉)
Beijing National Laboratory for Molecular Sciences (BNLMS), Centre for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
e-mail: jiangt@iccas.ac.cn

B. Han
e-mail: Hanbx@iccas.ac.cn

The epoxide ring of propylene oxide might open at either of the C–O bonds, to form primary or secondary alcohols. Compared to secondary alcohols, the primary alcohols (such as 2-methoxy-1-propanol), revealed the reproduction and developmental toxicity [20]. Therefore, the high selectivity to secondary alcohols is required for this process. The ring of propylene oxide might preferentially open at the least sterically hindered position over a basic catalyst leading to most secondary alcohol 1-methoxy-2-propanol. But an acid catalyst provides a mixture of secondary and primary alcohols, and the proportion of the isomers depends on the acid strength. So, the base catalysts attract much attention in the research and application.

In the past decades, a lot of homogenous base catalysts were exploited and showed high selectivity to secondary alcohol, but they had the drawbacks of separation, liquid waste treating and corrosion problems. Thus solid bases were developed to catalyze the synthesis of propylene glycol ether. Those heterogeneous catalysts included anionic double hydroxide clays [21], basic zeolites [22] and basic metal oxide [23–25].

Natural clay minerals are a type of environmentally benign material. Bentonite is a clay consisting predominantly of montmorillonite, which has layered structure, large surface areas, and cation exchange capacity. The special properties of bentonite make it a valuable material for a wide range of applications, such as environment and catalysis. Bentonite is potentially a good catalyst support. For example, ion-exchanged montmorillonite has been used to prepare excellent catalysts for the hydrogenolysis of glycerol [26]. A montmorillonite-enwrapped scandium has been used as a heterogeneous catalyst for Michael reaction [27]. Mesoporous SiO_2 is attractive supports due to their advantageous properties, such as excellent chemical and thermal stability, high porosity, large surface area, and high surface concentration of silanols. In this work, ionic liquid 1,1,3,3-tetramethylguanidium lactate ([TMG][Lac]) was immobilized on two kinds of solid supports, i.e. bentonite and SBA-15. The as-prepared materials were used as the basic and heterogeneous catalysts for preparing PGME from methanol and PO. Good yield and isomer selectivity were obtained over the two types of catalysts. The two catalysts can be separated with the products easily by centrifugation and reused without decrease in activity and selectivity.

2 Experimental

2.1 Materials

1,1,3,3-Tetramethylguanidine was purchased from Baigui Chemical Company (Shijiazhuang, China). The clay mineral used in this work is a smectite rich white bentonite provided by Zhejiang Sanding Scientific and Technology Co., Ltd., China. The composition of the clay was 58.98% SiO_2, 19.82% Al_2O_3, 3.73% MgO, 5.18% Na_2O, 0.42% K_2O, 0.87% CaO, 1.31% Fe_2O_3, 0.10% TiO_2, 0.74% P_2O_5, and 0.08% FeO. It was microporous and cation-rich (Na^+). The cation exchange capacity (CEC) of the bentonite was 99 mmol/100 g. (3-Mercaptopropyl) trimethoxysilane (3-MPTS) (98%) was obtained from Alfa. Pluronic triblock copolymer (EO20-PO70-EO20, P123) was obtained from Badische Anilin- and Soda-Fabrik (BASF). Other reagents and solvents were analytical grade and produced by Beijing Chemical Reagents Company. All chemicals were used as received.

2.2 Preparation of the Catalysts

2.2.1 *TMG/Bentonite*

[TMG][Lac] ionic liquid was prepared directly by neutralization of 1,1,3,3-tetramethylguanidine with lactic acid at room temperature [9]. Bentonite was treated with [TMG][Lac] to exchange the Na cations with the IL cations. 20.0 g of bentonite was dispersed in 150 mL of aqueous solution containing 4.87 g of [TMG][Lac], and stirred for about 6 h. Then the bentonite was separated by filtration, and treated with fresh IL aqueous solution again. The bentonite treated with IL aqueous solution was filtered, washed with a large amount of deionized water, dried at 378 K for 24 h and named as TMG/Bentonite.

2.2.2 *TMG/SBA-15*

The siliceous SBA-15 mesoporous material was synthesized according to the procedures described by Zhao et al. [28] using pluronic triblock copolymer (EO20-PO70-EO20, P123) as the structure-directing agent and tetraethyl orthosilicate (TEOS, 98%) as a source of silica. The triblock copolymer was dissolved in HCl aqueous solution (150 mL, 1.6 M) under stirring, after the required amount of TEOS was added to the solution at 308 K the solution was stirred for 20 h. The mixture was heated at 363 K for 24 h. After synthesis, the solid obtained was filtered, washed thoroughly with deionized water, dried at 373 K overnight and finally calcined at 773 K for 6 h to remove the organic template.

4 g of SBA-15 suspended in 25 g of dry toluene was refluxed and magnetically stirred for 1 h, under nitrogen atmosphere. To this suspension, excess 3-MPTS was added drop wise using a syringe. To ensure a complete covalent anchoring of the precursor over silica, the mixture was kept at reflux conditions for 48 h. Finally, the material was filtered, washed with toluene and ethanol and dried at 353 K

for 2 h. The oxidation of the mercapto propyl groups anchored on the silica surface to the corresponding sulphonic acids was carried out by treating 2 g of the sample with 20 mL of H_2O_2 (30 wt% in water) for 24 h. In order to confirm that all the sulphonic groups are protonated, the solid material was further acidified with 0.05 M H_2SO_4 for 2 h. The solid material obtained was then filtered, washed with water for several times and dried in air at 353 K for 24 h.

2 g of the sample and 100 g of deionized water was loaded into a 250 mL beaker, and the 5% aqueous solution of [TMG][Lac] was dropped into the beaker under stirring, until the pH of the solution in the beaker was basic. The solid was filtered off, washed with a large amount of deionized water, until the pH of the filtrate was about 7, and dried under vacuum at 353 K for 24 h to afford TMG/SBA-15.

2.3 Characterization of the Catalysts

FT-IR spectra of the samples were taken in the range of 4,000–400 cm^{-1} on Bruker Tensor 27 FT-IR spectrometer as KBr pellets. TG-DTA and DTG analysis of the catalysts were carried out on a TA Q50 using a platinum pan under (60 mL/min) atmosphere from ambient to 1,073 K with a heating rate of 20 K/min. The specific surface area, total pore volume and average pore diameter were measured by N_2 adsorption–desorption method using NOVA 1200 instrument (Quanta chrome). The samples were treated at 453 K for 3 h under vacuum and then the adsorption–desorption was conducted by passing nitrogen into the sample, which was kept under liquid.

2.4 Catalytic Performance Test

The catalytic performance of the catalysts was evaluated in a 6.5 mL batch reactor with molar ratio of methanol to PO of 1:1 to 5:1. After running at 373–413 K for a required time under magnetic stirring, the reactor was cooled down to room temperature. The products were analyzed by GC (Agilent 6820) equipped with a FID detector and a capillary column (SUPELCOWAX 10, 30 m in length, 0.25 mm in diameter) after centrifugal separation from the catalyst. 1-Propanol was used as the internal standard to calculate the amount of products. Yield of PGME (primary and second alcohols) is defined as the ratio of number of moles of PGME produced in the reaction to the total moles of PO initially added. Selectivity to 1-methoxy-2-propanol is defined as the ratio of number of moles of 1-methoxy-2-propanol to the number of moles of the two isomers.

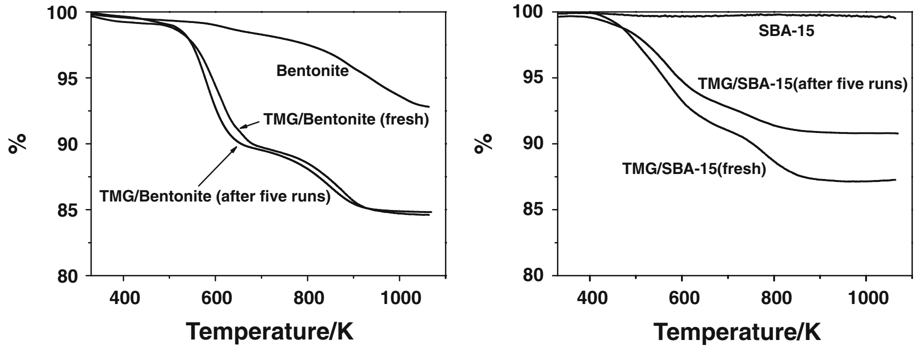
3 Results and Discussion

Before testing the catalytic activity of the catalysts, TMG/Bentonite and TMG/SBA-15 were characterized with FT-IR, and TG techniques to confirm the existence of TMG cations ($[TMG]^+$) on the surface of the catalyst. The presence of $[TMG]^+$ in the catalyst was supported by the fact that the catalysts contained organic compound (8.2 wt% for TMG/Bentonite, and 12.9 wt% for TMG/SBA-15) as determined by TGA (Fig. 1). The existence of the $[TMG]^+$ was also supported by the FT-IR analysis (Fig. 2). The specific peaks of TMG (TMG/Bentonite: 3242, 3418 ν(N–H), 2937 ν(C–H), 1622 ν(C=N), 1563 δ(N–H), 1463, 1422 δ(C–H) cm^{-1}; TMG/SBA-15: 3258, 3362 ν(N–H), 2905, 2944, 2980 ν(C–H), 1614 ν(C=N), 1658, 1570 δ(N–H), 1453, 1417 cm^{-1} δ(C–H)) can be observed in the spectra of the two catalysts.

Figure 3 is the N_2 adsorption–desorption isotherm of TMG/Bentonite and TMG/SBA-15. Because of the layered structure of bentonite, TMG/Bentonite shows a small surface area of 9.7 m^2/g, while TMG/SBA-15 shows a high surface area of 550 m^2/g due to its mesoporous structure. In addition, from TG analysis, the loading content of TMG cation was 0.7 mmol/g on TMG/Bentonite and 0.58 mmol/g on TMG/SBA-15, respectively.

The effect of the amount of the catalysts on the yield of PGME and the isomer selectivity to 1-methoxy-2-propanol is shown in Fig. 4. The PGME yield increases with the amount of TMG/Bentonite; while the yield arrives at the maximum when the amount of TMG/SBA-15 is 0.04 g.

Fig. 1 TG analysis of the supports, fresh and reused catalysts



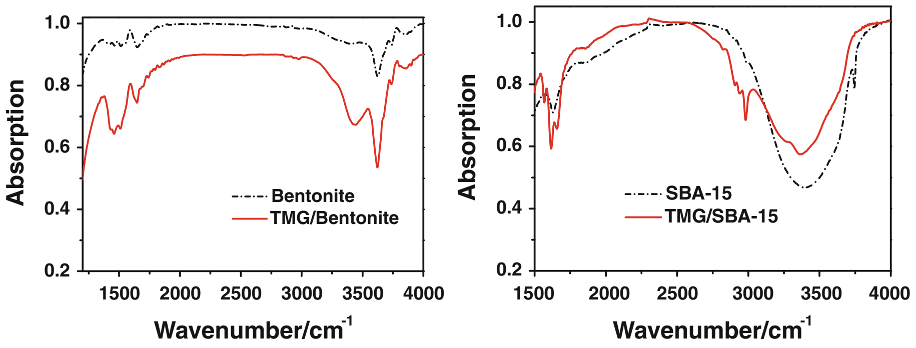


Fig. 2 FT-IR spectra of catalyst TMG/Bentonite and TMG/SBA-15

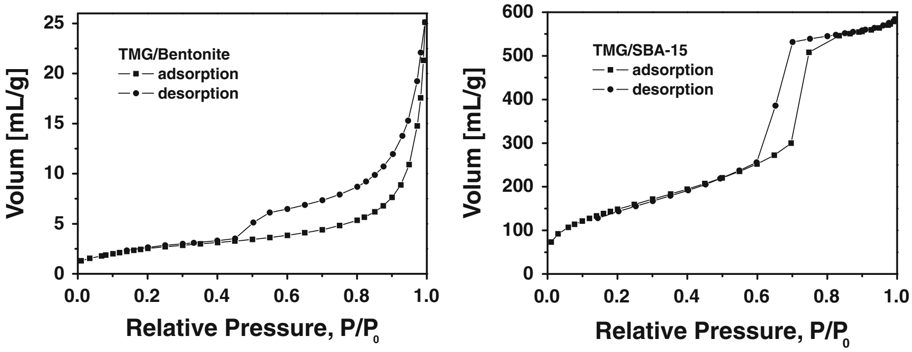


Fig. 3 N_2 adsorption–desorption isotherm of TMG/Bentonite and TMG/SBA-15

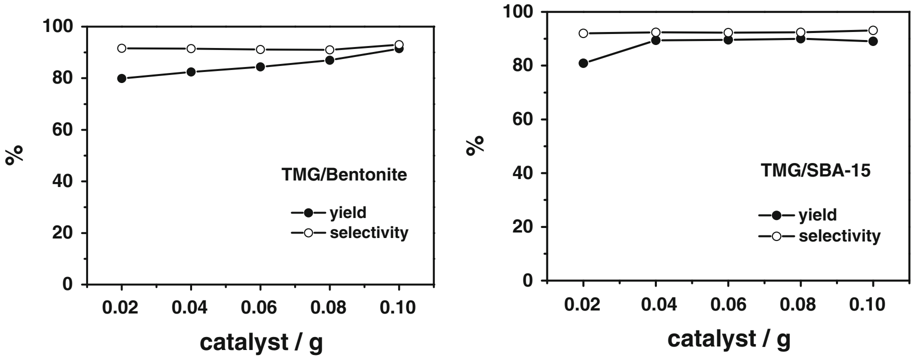


Fig. 4 The effect of the amount of the catalyst on the yield of PGME and isomer selectivity. Reaction conditions: PO, 20 mmol; MeOH/PO molar ratio, 3; reaction temperature, 383 K; reaction time, 3 h

The isomer selectivity does not change with the amount of catalysts over both catalysts, indicating that the supported TMG catalysts are effective for producing 1-methoxy-2-propanol isomer.

Figure 5 shows the influence of molar ratio of methanol to PO (MeOH/PO) on the yield of PGME and the isomer selectivity to 1-methoxy-2-propanol at 383 K for 3 h. With the increase of the molar ratio of MeOH/PO, PO could completely react with MeOH and the yield of PGME rapidly reaches a maximum value. When the molar ratio exceeds 3:1, the yield decreases slightly. The selectivity to 1-methoxy-2-propanol almost keeps constant over the two catalysts when changing the molar ratio of MeOH/PO.

As shown in Fig. 6, the dependence of the catalytic activity on the reaction temperature is different over the two catalysts. The effect of the reaction temperature on the activity of TMG/SBA-15 is not obvious. When increased the reaction temperature from 363 to 373 K, the yield is increased by 16% (72–88%, TMG/SBA-15). And then, the yield does not change with the increasing temperature. But the situation was different for the TMG/Bentonite. The yield is only 3% at 363 K and reaches the highest value at 383 K. The activity difference at low temperature might be due to the different of the surface area of two catalysts, which is important to the activity of the catalysts. The surface area of TMG/SBA-15 is almost sixty times of that

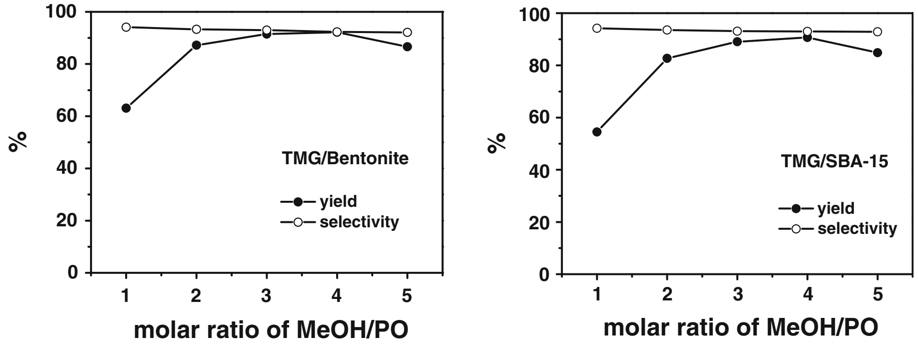


Fig. 5 The effect of molar ratio of MeOH/PO on the yield of PGME and the isomer selectivity. Reaction conditions: PO, 20 mmol; catalyst, 0.1 g; reaction temperature, 383 K; reaction time, 3 h

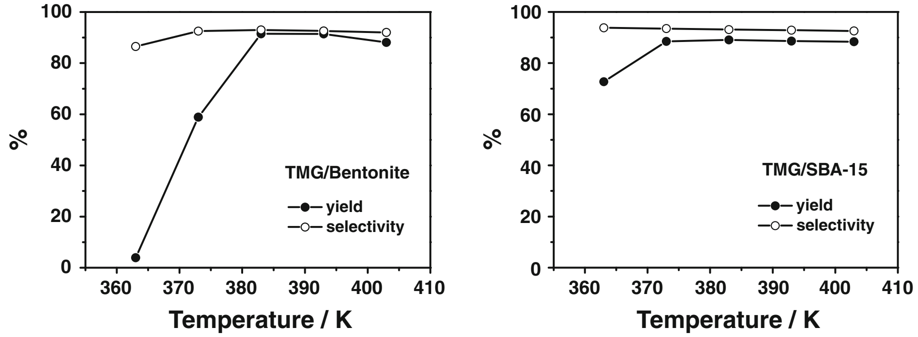


Fig. 6 The effect of the reaction temperature on the yield of PGME and the isomer selectivity. Reaction conditions: PO, 20 mmol; MeOH/PO molar ratio, 3; catalyst, 0.1 g; reaction time, 3 h

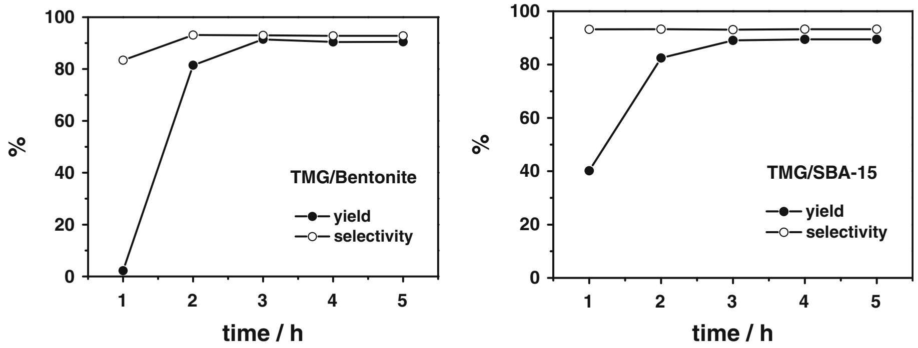


Fig. 7 The effect of reaction time on the yield of PGME and the isomer selectivity. Reaction conditions: PO, 20 mmol; MeOH/PO molar ratio, 3; catalyst, 0.1 g; reaction temperature, 383 K

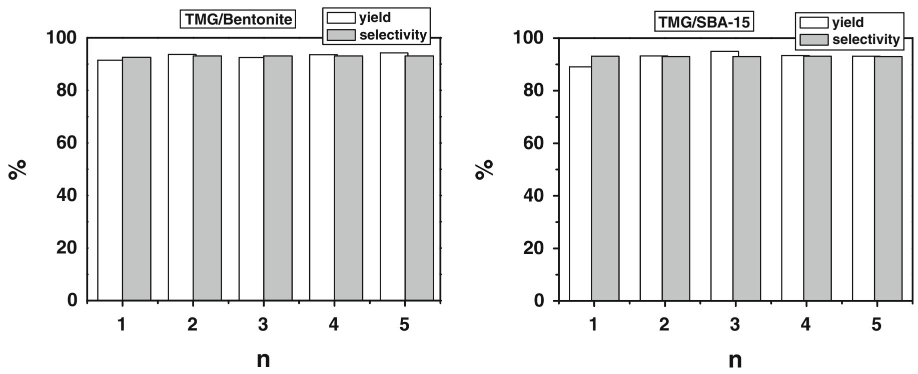


Fig. 8 Recycle of the catalyst TMG/Bentonite and TMG/SBA-15. Reaction conditions: PO, 20 mmol; MeOH/PO molar ratio, 3; catalyst, 0.1 g; reaction time, 3 h; temperature, 383 K

of TMG/Bentonite. So TMG/SBA-15 is more active than TMG/Bentonite at low temperature. At high temperature, the effect of temperature on the activity exceeds the effect of surface area, and the activity of two catalysts tends to the same. In addition, the effect of temperature on the selectivity is not obvious.

The dependence of the yield of PGME and the selectivity to 1-methoxy-2-propanol on the reaction time is presented in Fig. 7. In a relatively short reaction time, the conversion of PO is incomplete and the PGME yield is low. It can be seen that the maximum yield could be achieved at 3 h and no further increase in the yields of PGME is observed with prolonged reaction time over the two catalysts. But the yield over TMG/SBA-15 is higher than that over TMG/Bentonite when the reaction time was 1 h. This might be attributed to the enormous difference of the surface area of the two supports. The high surface area favors the contact of reactants on the catalyst surface. This effect is especially obvious at short reaction time.

The reusability of TMG/Bentonite and TMG/SBA-15 were examined at the optimized reaction conditions and the results are shown in Fig. 8. The yield of PGME and the selectivity to 1-methoxy-2-propanol do not decrease after five recycle, indicating that both of the catalysts are recyclable. The good stability can also be supported by the results of TG analysis that the catalysts are stable below about 423 K. The TG results indicated that there was not ionic liquid leaching for TMG /Bentonite after five runs. For TMG/SBA-15, about 30% ionic liquid was leached after five runs.

4 Conclusion

The ionic liquid 1,1,3,3-tetramethylguanidium lactate was immobilized on two types of solid supports, bentonite and SBA-15, with different method. The obtained materials were proved to be excellent heterogeneous catalysts for the reaction of methanol with PO to produce PGME. 1-Methoxy-2-propanol was the predominant product. At the optimized reaction conditions, the yield of PGME and the selectivity to 1-methoxy-2-propanol over TMG/Bentonite are as high as 89 and 93%, respectively. The two catalysts can be recovered easily and reused for at least four cycles without decrease in activity and selectivity.

Acknowledgments The authors are grateful to the financial supports from the Ministry of Science and Technology of China (2006CB202504), Chinese Academy of Sciences (KJCX2.YW.H16) and National Natural Science Foundation of China (20932002, 20733010, 20633080).

References

1. Welton T (1999) Chem Rev 99:2071
2. Earle MJ, Seddon KR (2000) Pure Appl Chem 72:1391
3. Wasserscheid P, Keim W (2000) Angew Chem Int Ed 39:3773
4. Sheldon R (2001) Chem Commun 23:2399
5. Dupont J, de Souza RF, Auarez PAZ (2002) Chem Rev 102:3667
6. Herrenmann WA (2001) Angew Chem Int Ed 41:1290
7. Mehnert CP, Dispenziere NC, Cook RA (2002) Chem Commun 15:1610
8. Zhao D, Fei Z, Geldbach TJ, Scopelliti R, Dyson PJ (2004) J Am Chem Soc 126:15876
9. Gao H, Han B, Li J, Jiang T, Liu Z, Wu W, Chang Y, Zhang J (2004) Synth Commun 34:3083
10. Jiang T, Gao H, Han B, Zhao G, Chang Y, Wu W, Gao L, Yang G (2004) Tetrahedron Lett 45:2699
11. Zhu A, Jiang T, Wang D, Han B, Liu L, Huang J, Zhang J, Sun D (2005) Green Chem 7:514
12. Zhu A, Jiang T, Han B, Huang J, Zhang J, Ma X (2006) New J Chem 30:736
13. Huang J, Jiang T, Gao H, Han B, Liu Z, Wu W, Chang Y, Zhao G (2004) Angew Chem Int Ed 43:1397
14. Ma XM, Zhou YX, Zhang JC, Zhu AL, Jiang T, Han BX (2008) Green Chem 10:59
15. Wu W, Han B, Gao H, Liu Z, Jiang T, Huang J (2004) Angew Chem Int Ed 43:2415
16. Xie H, Duan H, Li S, Zhang S (2005) New J Chem 29:1199
17. European Chemical Industry Ecology and Toxicological Center Report (1982) No. 4
18. Woods G (1990) The ICI polyurethanes book, 2nd edn. Wiley, Chichester
19. Parker RE, Isaacs NS (1959) Chem Rev 59:737
20. European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) (1995) The toxicology of glycol ethers and its relevance to man. Technical Report No. 64:1
21. Martin PA, William T, Malama C (1992) Process for the preparation of glycol ethers. US Patent 5,110,992
22. Smith WJ, Malherbe FC (2001) Synthesis of glycol ethers. US Patent 6,291,720B1
23. Liu SG, Zhang XL, Li JP, Zhao N, Wei W, Sun YH (2008) Catal Commun 9:1527
24. Zhang WY, Wang H, Wei W, Sun YH (2005) J Mol Catal A Chem 231:83
25. Zhang WY, Wang H, Li QB, Dong QN, Zhao N, Wei W, Sun YH (2005) Appl Catal A Gen 294:188
26. Jiang T, Zhou Y, Liang S, Liu H, Han B (2009) Green Chem 11:1000
27. Kawabata T, Mizugaki T, Ebitani K, Kaneda K (2003) J Am Chem Soc 125:10486
28. Zhao D, Huo Q, Feng J, Chmelka BF, Stucky GD (1998) J Am Chem Soc 120:6024