

A new route for the synthesis of propylene oxide from bio-glycerol derived propylene glycol

Zhengxi Yu,^{ab} Lei Xu,^a Yingxu Wei,^a Yingli Wang,^{ab} Yanli He,^a Qinghua Xia,^{ac} Xinzhi Zhang^{ad} and Zhongmin Liu^{*a}

Received (in Cambridge, UK) 15th April 2009, Accepted 5th May 2009

First published as an Advance Article on the web 27th May 2009

DOI: 10.1039/b907530e

The synthesis of propylene oxide from propylene glycol, a derivative of bio-glycerol, was firstly realized in the presence of alkali-loaded silica catalysts to achieve 44% conversion and 70% selectivity.

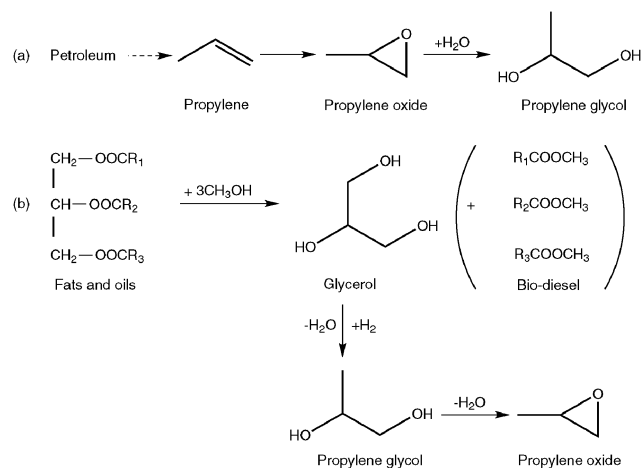
Propylene oxide (PO), an important bulk chemical intermediate with a global annual capacity of 7 million metric tons,¹ is widely used for manufacturing of polyurethane, unsaturated resins, surfactants and other products. PO is traditionally produced by two routes, namely the chlorohydrin and Halcon (hydroperoxide) processes.² In the chlorohydrin process, propylene is reacted with chlorine, water and calcium hydroxide to generate PO and chlorinated by-products such as dichloropropane and CaCl₂, which result in serious equipment corrosion and environment pollution. The Halcon process uses either *tert*-butyl or ethylbenzene hydroperoxides as the oxidant to epoxidize propylene, and generates *tert*-butanol or styrene (3–4 kg of *tert*-butanol or 2.4 kg of styrene per kg of propylene oxide) as co-products. In order to eliminate pollution and co-products, researchers have conducted many efforts on direct oxidation of propylene by using a greener oxidant, hydrogen peroxide (H₂O₂),³ which has undergone significant progress after the discovery of titanium silicalite (TS-1) as an effective catalyst support.⁴ Recently, it was reported that Dow and BASF announced the construction of the first commercial PO plant using pre-manufactured H₂O₂ to epoxidize propylene.¹

However, all the above PO production technologies consume petrochemically-derived propylene (Scheme 1(a)). As the supply and price of oil show an unstable tendency, daily exhaustion of petroleum resource calls for the chemical production from alternative resources. With the rapid development of the bio-diesel industry, glycerol of renewable origin, as a by-product of bio-diesel production, seems to be an attractive option as a new feedstock. Glycerol is known to react with hydrogen to form propylene glycol (PG) and water *via* consecutive dehydration and hydrogenation.⁵ Schuster and Eggersdorfer⁶ have patented a method to produce propanediols

using a catalyst containing cobalt, copper, manganese, molybdenum and an inorganic polyacid with 95.8% yield of PG at 250 bar and 523 K. Cui and Chen *et al.*⁷ described the preparation of PG through the hydrogenation of glycerol over CuO/SiO₂ catalysts with 95.4% yield of PG at 80 bar and 463 K. Dasari *et al.*⁸ reported the efficiency of copper chromite catalysts for the hydrogenolysis of glycerol to PG (85.0% selectivity and 54.8% conversion) at 473 K and 1.4 MPa (a mild hydrogen pressure). Recently, BASF⁹ has announced the application of the PG production technique from bio-glycerol and the construction timetable of the first industrial unit with a capacity of 100 kt a⁻¹ in the Antwerp–Ludwigshafen chemical industry area. Based on this mature technology of glycerol hydrogenolysis to PG, the present study firstly reports a new route to produce PO from glycerol *via* the PG intermediate (Scheme 1(b)). Hopefully, the use of bio-glycerol feedstock as the starting material will notably reduce the consumption of petroleum to some extent.

PG could be obtained by a traditional hydrolysis of PO with acid or base catalysts,¹⁰ while its reverse process, the PO production from the cyclodehydration of PG is rather difficult and much less studied. In 1978, Fouquet *et al.*¹¹ claimed a technology for the preparation of PO from PG or a mixture containing PG and its mono- and diesters, in which the PG was manufactured *via* its esters, obtained by acyloxylation of propylene.

In the present work, the selectively catalytic transformation of PG to PO is carried out over a series of alkali-loaded silica



Scheme 1 Comparison of the reaction routes to propylene oxide and propylene glycol starting from propylene or glycerol.

^a Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P.R. China. E-mail: liuzm@dicp.ac.cn; Fax: + 86-411-84691570; Tel: + 86-411-84685510

^b Graduate University of Chinese Academy of Sciences, Beijing 100049, P.R. China

^c Ministry-of-Education Key Laboratory for the synthesis and Application of Organic Functional Molecules, School of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, P.R. China

^d China National Petroleum Corporation, Beijing 100007, P.R. China

Table 1 Propylene glycol conversions over different catalysts^a

Entry	Catalyst ^b	<i>X</i> ^c (%)	Yield ^d (%)	<i>S_i</i> ^e (%)					
				PO	Propionaldehyde	Acetone	Allyl alcohol	Acetol	<i>Di</i> -PG
1	Al ₂ O ₃	97.27	0	0	57.50	36.36	6.14	0	0
2	MgO	24.61	0.56	2.28	3.35	3.78	0	90.59	0
3	SiO ₂ ^f	13.19	0	0	57.01	7.96	7.07	0	0
4	Li(1.5)SiO ₂	11.15	4.47	40.10	30.38	15.57	1.68	3.80	8.47
5	Na(1.5)SiO ₂	19.53	11.29	57.79	14.31	10.64	2.87	0	14.39
6	K(0.75)SiO ₂	14.82	8.68	58.59	8.00	5.77	3.91	0	23.74
7	K(1.5)SiO ₂	33.30	23.21	69.70	6.93	5.62	3.72	0.83	13.21
8	K(2.25)SiO ₂	39.56	27.60	69.77	7.71	6.45	4.34	1.38	10.26
9	K(3)SiO ₂	44.34	31.16	70.28	7.93	7.19	4.76	1.18	8.66
10	K(3.75)SiO ₂	36.12	26.11	72.28	6.98	6.60	4.24	1.28	8.62
11	Cs(0.075)SiO ₂	3.51	0.78	22.17	35.26	14.62	5.01	10.00	12.94
12	Cs(0.375)SiO ₂	22.98	13.82	60.16	8.70	4.80	4.30	1.32	20.71
13	Cs(0.75)SiO ₂	51.91	32.23	62.08	9.00	6.04	6.61	1.65	14.62
14	Cs(1.5)SiO ₂	13.22	9.67	73.12	7.01	4.75	4.10	5.48	5.54

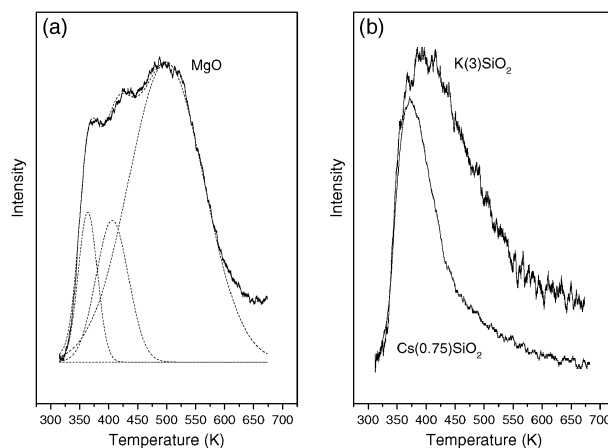
^a Reaction conditions: temperature = 673 K, reaction time = 3 h, N₂ = 18 ml min⁻¹, PG WHSV = 1.7 h⁻¹, 1 g catalyst. ^b Values in parentheses denote the amount of alkali metal loaded on SiO₂. ^c *X* = conversion. ^d Yield of PO. ^e *S_i* = Carbon selectivity. ^f 2-Ethyl-4-methyl-1,3-dioxolane formed with 27.97% selectivity.

catalysts in a fixed-bed reactor (7 mm i. d.). Al₂O₃ (Fushun Catalyst Co.) and MgO (self-synthesized), with specific surface area of 311 and 49.5 m² g⁻¹, respectively, were also tested for comparison. All the products are quantitatively analyzed by a gas chromatograph equipped with an FID detector and the results are detailed in Table 1.

Over the solid acid catalyst Al₂O₃, the electrophilic dehydration of PG occurred mainly to generate propionaldehyde, acetone and allyl alcohol but not to form the target product PO at all (Table 1, entry 1). Over the catalyst MgO, known as a medium-strong solid base catalyst, PG was mainly transformed to acetol *via* dehydrogenation with a high selectivity of 90.59%, while only 2.28% of PO was detected.

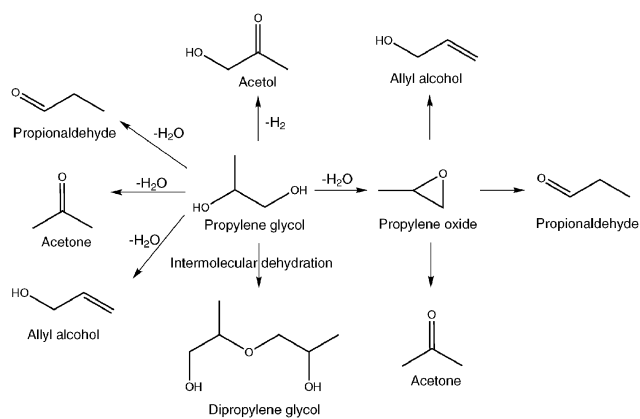
To improve the PO selectivity, a series of alkali-loaded silica catalysts were prepared by impregnating the porous silica with a nitrate solution of alkali metal (alkali metal = Li, Na, K and Cs), followed by drying and calcination at 823 K for 6 h. The catalytic results show that porous silica without alkali metal was almost inactive for the PO formation (Table 1, entry 3); however, the catalyst modified with alkali metal nitrate (Li, Na, K and Cs) by impregnation gave rise to a remarkable increase of the PO selectivity. With increasing the content of K or Cs, the selectivity to PO was dramatically improved. When the loading of alkali metal reached 1.5 mmol g⁻¹ (Table 1, entries 4, 5, 7 and 14), Cs(1.5)SiO₂ exhibited the highest selectivity to PO (73.12%) and K(1.5)SiO₂ achieved the highest yield of PO (23.21%). The conversion of PG first increased to a maximum of 44.34% (K(3)SiO₂) or 51.91% (Cs(0.75)SiO₂), and then decreased with the further increase of K or Cs loading.

The CO₂-TPD measurements clearly show the difference of surface basicity between MgO and alkali-loaded silica catalysts. The appearance of three CO₂ desorption peaks at 364, 406 and 500 K reflects three kinds of base sites on the surface of MgO (Fig. 1(a)). Note that base sites with moderate strength appear at 500 K as the major CO₂ desorption. For K(3)SiO₂ and Cs(0.75)SiO₂, the CO₂ desorption occurs in the temperature range of 363–423 K (Fig. 1(b)), implying the weak

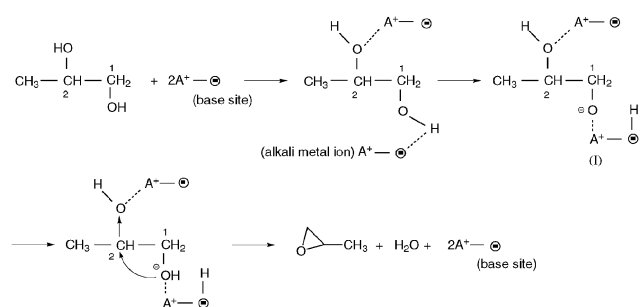
**Fig. 1** CO₂-TPD profiles of (a) MgO, (b) K(3)SiO₂ and Cs(0.75)SiO₂.

basicity of the two catalysts. Over solid acid catalyst of Al₂O₃, PG readily undergoes electrophilic dehydrations to generate the corresponding carbonyl compounds and unsaturated alcohols including propionaldehyde, acetone and allyl alcohol, in which carbonyl compounds result from the pinacol rearrangement through the 1,2-shift of hydride anions or 1,2-elimination of unsaturated alcohols.¹² Over solid base catalyst of MgO, PG is mainly transformed to acetol by dehydrogenation due to the dominant moderate strength base sites on the surface. Over the alkali-loaded silica catalysts (*e.g.* K(3)SiO₂ and Cs(0.75)SiO₂), PO is the main product, suggesting that the weak base sites supported by silica probably play crucial roles in the intramolecular dehydration of PG to PO.

A network of PG transformation is illustrated in Scheme 2. It is well known that the ether production requires the presence of acid–base site pairs.¹³ Thus, the formation of *di*-PG over alkali-loaded silica may be due to the co-interaction between acid sites on porous silica and base sites contributed by alkali metal. This has been confirmed by the results that



Scheme 2 Reaction pathways for PG transformation.



Scheme 3 Plausible mechanism of PG intramolecular dehydration to PO over alkali-loaded silica catalysts.

the selectivity to *di*-PG first increases to a maximum, and then decreases with the increase of alkali loadings. Other by-products, such as propionaldehyde, acetone and allyl alcohol, may be formed *via* the PO isomerization in addition to the PG transformation.¹⁴

Based on the above results and the formation mechanisms of other ethers,¹³ the PO formation mechanism catalyzed by alkali-loaded silica can be proposed as follows (see Scheme 3). On the surface of alkali-loaded silica, the adsorbed PG molecule is converted to an effective nucleophile (structure I) *via* the abstracting of the primary hydroxyl proton by the base site; at the same time the secondary hydroxyl group becomes a good leaving group. Subsequently, the C² atom is attacked by the nucleophilic C¹-O⁻, accompanied with the dehydroxylation of the secondary OH group (the concerted nucleophilic substitution), to produce PO and water.

In summary, we have proposed a novel and sustainable route for the production of PO from bio-glycerol *via* the PG intermediate. Alkali-loaded silicas are active and selective catalysts for this process. The weak base sites may play crucial roles in the intramolecular dehydration of PG to PO.

Notes and references

- 1 A. H. Tullo and P. L. Short, *Chem. Eng. News*, 2006, **84**, 22.
- 2 (a) D. L. Trent, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, New York 4th edn, 1996, vol. 20, p. 271; (b) G. Wegener, M. Brandt, L. Duda, J. Hofmann, B. Kleszczewski, D. Koch, R. J. Kumpf, H. Orzesek, H. G. Pirkl, C. Six, C. Steinlein and M. Weisbeck, *Appl. Catal., A*, 2001, **221**, 303.
- 3 (a) T. Danciu, E. J. Beckman, D. Hancu, R. N. Cochran, R. Grey, D. M. Hajnik and J. Jewson, *Angew. Chem., Int. Ed.*, 2003, **42**, 1140; (b) A. K. Sinha, S. Seelan, S. Tsubota and M. Haruta, *Angew. Chem., Int. Ed.*, 2004, **43**, 1546; (c) Q. L. Chen and E. J. Beckman, *Green Chem.*, 2008, **10**, 934; (d) Z. W. Xi, N. Zhou, Y. Sun and K. L. Li, *Science*, 2001, **292**, 1139; (e) B. Chowdhury, J. J. Bravo-Suarez, M. Date, S. Tsubota and M. Haruta, *Angew. Chem., Int. Ed.*, 2006, **45**, 412; (f) R. Meiers, U. Dingerissen and W. F. Holderich, *J. Catal.*, 1998, **176**, 376; (g) N. Yap, R. P. Andres and W. N. Delgass, *J. Catal.*, 2004, **226**, 156.
- 4 (a) M. Taramasso, G. Perego and B. Notari, *US Pat.*, 4 410 501, 1983; (b) M. Taramasso, G. Manara, V. Fattore and B. Notari, *US Pat.*, 4 666 692, 1987; (c) M. G. Clerici, G. Bellussi and U. Romano, *J. Catal.*, 1991, **129**, 159.
- 5 (a) B. Casale and A. M. Gomez, *US Pat.*, 5 214 219, 1993; (b) B. Casale and A. M. Gomez, *US Pat.*, 5 276 181, 1994; (c) T. Haas, A. Neher, D. Arntz, H. Klenk and W. Girke, *US Pat.*, 5 426 249, 1995; (d) D. J. Miller, J. E. Jackson and S. Marincean, *US Pat.*, 2008/0242898 A1, 2008; (e) A. Perosa and P. Tundo, *Ind. Eng. Chem. Res.*, 2005, **44**, 8535; (f) J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel and C. Rosier, *Green Chem.*, 2004, **6**, 359; (g) I. Furikado, T. Miyazawa, S. Koso, A. Shimao, K. Kunimori and K. Tomishige, *Green Chem.*, 2007, **9**, 582; (h) C. Montassier, J. M. Dumas, P. Granger and J. Barbier, *Appl. Catal., A*, 1995, **121**, 231; (i) T. Miyazawa, S. Koso, K. Kunimori and K. Tomishige, *Appl. Catal., A*, 2007, **329**, 30; (j) E. D'Hondt, S. Van de Vyver, B. F. Sels and P. A. Jacobs, *Chem. Commun.*, 2008, 6011.
- 6 L. Schuster and M. Eggersdorfer, *US Pat.*, 5 616 817, 1997.
- 7 F. Cui, J. Chen, C. Xia, Z. Huang, X. Zhang and J. Tong, *Chin. Pat.*, CN 101195557A, 2008.
- 8 M. A. Dasaria, P. P. Kiatsimkula, W. R. Sutterlin and G. J. Suppes, *Appl. Catal., A*, 2005, **281**, 225.
- 9 J. Shen, *Chin. J. Petrol. Process. Petrochem.*, 2008, **39**, 25.
- 10 (a) J. H. Robson and G. E. Keller, *US Pat.*, 4 551 566, 1985; (b) T. Masuda, K. Asano, N. Hori and S. Ando, *US Pat.*, 4 937 393, 1990; (c) R. D. Best, J. A. Collier, B. T. Keen and J. H. Robson, *US Pat.*, 4 982 021, 1991; (d) P. Bassler, H. G. Goebbel, J. H. Teles and P. Rudolf, *US Pat.*, 7 084 310, 2006; (e) A. Lundin, I. Panas and E. Ahlberg, *J. Phys. Chem. A*, 2007, **111**, 9087.
- 11 G. Fouquet, F. Merger and K. Baer, *Ger. Pat.*, DE 2709440 A1, 1978.
- 12 (a) I. Bucsí, A. Molnár and M. Bartók, *Tetrahedron*, 1994, **50**, 8195; (b) B. Torok, I. Bucsí, T. Beregszászi, I. Kapocsi and A. Molnár, *J. Mol. Catal. A: Chem.*, 1996, **107**, 305.
- 13 (a) B. Shi and B. H. Davis, *J. Catal.*, 1995, **157**, 359; (b) C. C. Vanesa, M. A. Rosa, I. Sobczak and M. Ziolek, *Appl. Catal., A*, 2006, **303**, 121; (c) S. Delsarte, M. Florea, F. Mauge and P. Grange, *Catal. Today*, 2006, **116**, 216; (d) S. Delsarte and P. Grange, *Appl. Catal., A*, 2004, **259**, 269.
- 14 (a) F. Dubnikova and A. Lifshitz, *J. Phys. Chem. A*, 2000, **104**, 4489; (b) A. Lifshitz and C. Tamburu, *J. Phys. Chem.*, 1994, **98**, 1161.