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

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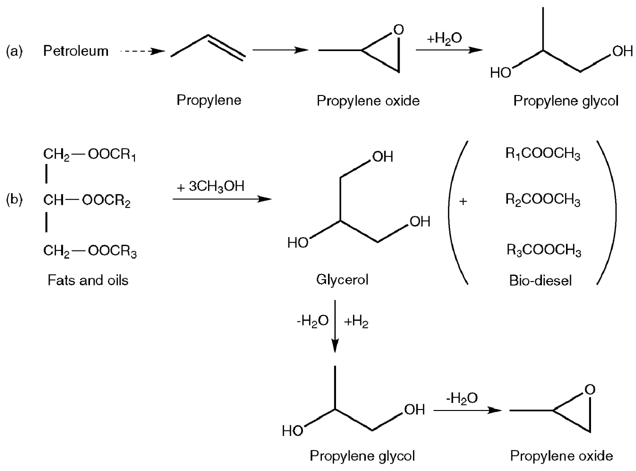
The synthesis of propylene oxide from propylene glycol, a derivative of bio-glycerol, was firstly realized in the presence of alkali-loaded silica catalysts to achieve 44% conversion and 70% selectivity.

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 $CaCl_2$, 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 (H_2O_2),[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 H_2O_2 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 Eggersdorfer[6] 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/SiO_2 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, BASF[9] 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.

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Table 1 Propylene glycol conversions over different catalysts[a]

				S_i^e (%)					
Entry	Catalyst[b]	X^c (%)	Yield[d] (%)	PO	Propionaldehyde	Acetone	Allyl alcohol	Acetol	*Di*-PG
1	Al_2O_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, N_2 = 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 SiO_2. [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.). Al_2O_3 (Fushun Catalyst Co.) and MgO (self-synthesized), with specific surface area of 311 and 49.5 m^2 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 Al_2O_3, 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)SiO_2 exhibited the highest selectivity to PO (73.12%) and K(1.5)SiO_2 achieved the highest yield of PO (23.21%). The conversion of PG first increased to a maximum of 44.34% (K(3)SiO_2) or 51.91% (Cs(0.75)SiO_2), and then decreased with the further increase of K or Cs loading.

The CO_2-TPD measurements clearly show the difference of surface basicity between MgO and alkali-loaded silica catalysts. The appearance of three CO_2 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 CO_2 desorption. For K(3)SiO_2 and Cs(0.75)SiO_2, the CO_2 desorption occurs in the temperature range of 363–423 K (Fig. 1(b)), implying the weak basicity of the two catalysts. Over solid acid catalyst of Al_2O_3, 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)SiO_2 and Cs(0.75)SiO_2), 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.

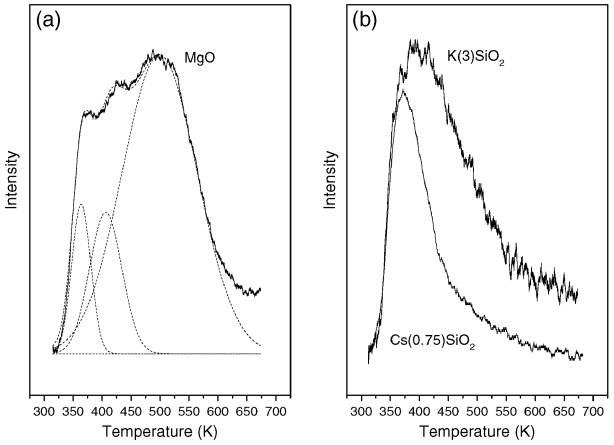
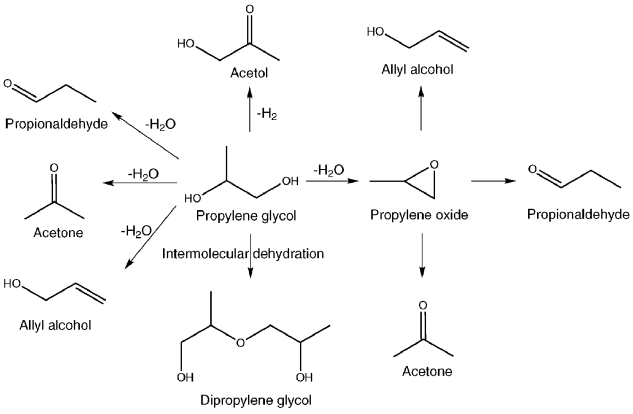
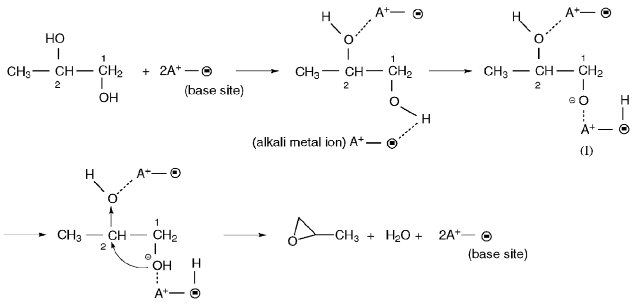


Fig. 1 CO_2-TPD profiles of (a) MgO, (b) K(3)SiO_2 and Cs(0.75)SiO_2.

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 C^2 atom is attacked by the nucleophilic C^1–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.

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