The synthesis of propylene glycol and ethylene glycol from glycerol using Raney Ni as a versatile catalyst†

An-Yuan Yin,‡ Xiu-Ying Guo,‡ Wei-Lin Dai* and Kang-Nian Fan

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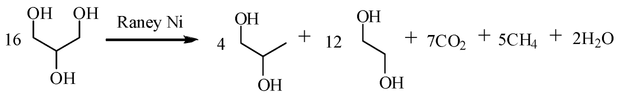
A new energy-efficient and atom-economical catalytic route for the direct catalytic synthesis of propylene glycol and ethylene glycol from glycerol under milder reaction conditions is presented. The one-pot aqueous-phase process is based on Raney Ni as a versatile catalyst.

Propylene glycol (PG) and ethylene glycol (EG), used as high value-added speciality chemical intermediates, are widely used for manufacturing polyester fibers, unsaturated polyester resins, antifreeze, pharmaceuticals and other important products.[1] At present, these two diols are mainly produced from the hydration of corresponding epoxy alkanes, which are commonly derived from a petrochemical approach.[2] However, as crude oil resource shrinks, synthesis of the two diols from biomass glycerol attracts more and more interest.[3] With the rapid development of the bio-diesel industry by transesterification of seed oils with methanol, glycerol of renewable origin, as a by-product of bio-diesel production, seems to be an attractive option as a new feedstock.[4] Glycerol, as a nontoxic, edible, biodegradable and low-cost polyfunctional molecule, has been regarded as one of the building blocks in the biorefinery industry. Various conversions of glycerol into value-added chemicals, including selective oxidation, esterification, hydrogenolysis, dehydration and reforming, have received significant attention during the last few decades because the cost of glycerol as a by-product is projected to decrease significantly as biodiesel production increases.[5]

On the whole, the large surplus of glycerol in association with its high functionalization makes it one of the most promising platform chemicals of the near future. Also, converting glycerol into value-added products provides an alternative for glycerol disposal and for its surplus problems. Among the various glycerol transformations, much attention has been paid to synthesizing propanediol and EG *via* the hydrogenolysis of glycerol. Catalysts containing an active copper compound such as Cu-chromite, Cu-ZnO, Cu-SiO_2 or Cu-Al_2O_3 are active in glycerol hydrogenation at temperature between 423–593 K and pressure between 10 and 25 MPa.[6] Under similar reaction conditions, a catalyst system containing Co, Cu, Mn, Mo as well as inorganic polyacids, leads to nearly quantitative conversions with selectivity of >95%.[7] Another way of converting glycerol to PG is the use of ruthenium in combination with acids or ion-exchange resins, which enables slightly milder reaction conditions, but also lower conversions and selectivities.[8] As in the case of Rh as a catalyst, reaction conditions are relatively mild.[9] The use of Rh as a catalyst component in a multimetallic catalyst leads to conversions up to 80% with selectivities of >30% at a temperature higher than 393 K and 8 MPa hydrogen pressure.[9] In all the cases, either selectivity was low or high pressure, high temperature and very complex catalytic systems were required.

Although the hydrogenolysis of glycerol opened up a new approach to synthesize PG and EG, high hydrogen pressure (8 MPa), high temperature (473 K) and use of expensive noble metal catalysts are still key factors to limit its further application in industry. The reaction mechanism on metallic metal is accepted as glycerol dehydration under the acid or base environment firstly, then hydrogenation to PG over metal catalyst.[10] Aqueous phase reforming (APR) can be used to convert glycerol with water into H_2 and CO_2 at temperatures near 500 K over metallic catalysts.[3] Importantly, the selectivity towards H_2 can be controlled by altering the nature of the catalytically active metal sites (*e.g.*, Pt) and metal-alloy (*e.g.*, Ni-Sn) components, and by choice of catalyst support to obtain higher production of hydrogen at higher pressure (3–4 MPa) and slightly lower temperature (398 K), which is thermodynamically favorable to the water-gas-shift reaction.[11] Based on the above reaction process, the direct catalytic conversion of glycerol to PG and EG with water can be carried out by combining the APR process and the hydrogenolysis of glycerol using the hydrogen produced *in situ* by the APR process, which can not only save energy but also allow easy control of the reaction under mild conditions.

The present study firstly reports a new route to produce PG and EG from glycerol under 0.1 MPa nitrogen atmosphere conditions (Scheme 1). In particular, Raney Ni is strongly active for this glycerol catalytic conversion process and the products are easy to separate from the reaction system without further purification.



Scheme 1 Reaction approach to propylene glycol and ethylene glycol derived from glycerol reforming.

In the present work, the chemo-selectively catalytic conversion of glycerol to PG and EG is carried out over commercial

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Department of Chemistry & Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Fudan University, Shanghai, 200433, P. R. China. E-mail: wldai@fudan.edu.cn; Fax: (+86-21) 55665572; Tel: (+86-21) 55664678

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‡ These authors contributed equally to this work.

Table 1 Effect of reaction temperature on the catalytic performance over Raney Ni catalyst[a]

			Selectivity[c] (%)		
T/K	Conversion (%)	Yield[b] (%)	PG	EG	Ethanol
433	49.2	36.3	37.2	61.8	1.0
443	64.3	41.1	42.1	56.3	1.6
453	100	58.2	43.0	55.0	2.0
463	100	51.4	43.9	51.5	4.6
473	100	47.2	48.7	44.5	6.8

[a] Reaction conditions: 30 ml aqueous glycerol (10 wt%), catalyst (1 g), N_2 (0.1 MPa), 1 h. [b] Total yield of liquid products. [c] C-based composition of liquid products/mol%.

Raney Ni catalysts (A.R., Sinopharm Chemical Reagent Ltd.) in a stainless steel autoclave. Thirty millilitres of an aqueous solution of glycerol (10 wt%) was used as the reactant. No additives, including alkaline, were needed. All the products are quantitatively analyzed by a gas chromatograph equipped with an FID detector.

It is interesting to find that a high pressure of hydrogen was not favorable to this reaction. Under 3 MPa H_2, only 50% conversion of glycerol was observed. On the contrary, air is not good for this reaction, since fresh Raney Ni is very active and it is not safe to carry out this reaction under air atmosphere. Inert atmosphere at ambient pressure was found to show unique advantages in this process. Thus, we choose 0.1 MPa N_2 as the optimal atmosphere. Table 1 shows the effect of reaction temperature on the catalytic performance of glycerol conversion over Raney Ni catalyst. As can be seen, 100% glycerol conversion and 57.0% yield of total diols could be obtained at 453 K. Compared with the theoretical yield of the diols (75%), this result is rather high over the Raney Ni catalyst. Although 100% glycerol conversion could still be retained with further increasing of the reaction temperature, the total yield of diols decreased. This may be a result of the further hydrogenolysis of the diols and the methanation under higher reaction temperature. Based on the distribution of the products upon the variation of reaction temperatures, higher temperature is helpful to the cleavage of the C–O bond while inhibiting the cleavage of the C–C bond, and further degradation of the diols could happen at higher reaction temperatures.

To obtain an insight into the origin of the reaction processes, we examined the course of the conversion of glycerol aqueous solution over time. The time course of the products distribution is given in Table 2. As can be seen, the glycerol conversion and the total yield of the diols increased with prolonging of the reaction time; however, the yield of diol would decrease upon further extending of the reaction time. Based on the distribution of the products, extending the reaction time could lead to further C–C cleavage, and as a result, PG would further degrade to EG.

Table 2 Effect of reaction time on the catalytic performance over Raney Ni catalyst[a]

			Selectivity[c] (%)		
Time/h	Conversion (%)	Yield[b] (%)	PG	EG	Ethanol
0.5	74.2	42.0	26.2	71.4	2.4
1.0	100	58.2	43.0	55.0	2.0
1.5	100	47.4	42.2	54.9	2.9
2.0	100	41.1	29.2	68.1	2.7

[a] Reaction conditions: 30 ml aqueous glycerol (10 wt.%), catalyst (1 g), N_2 (0.1 MPa), 453 K. [b] Total yield of liquid products. [c] C-based composition of liquid products/mol%.

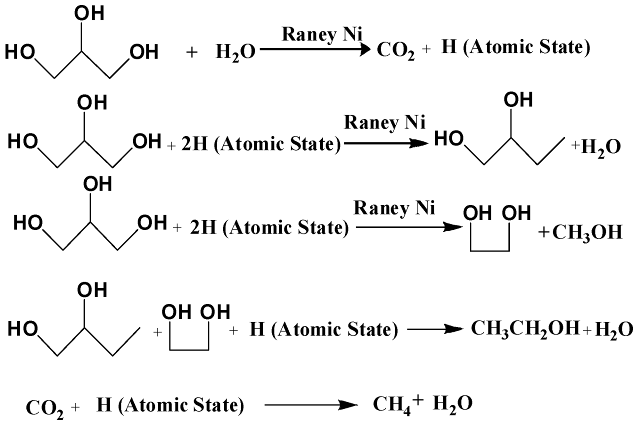
Table 3 Results of the reactions of various compounds[a]

			Selectivity[c] (%)		
Reactant	Conversion (%)	Yield[b] (%)	PG	EG	Ethanol
PG	35	5.5	0	0	100
EG	64	19	0	0	100

[a] Reaction conditions: 453 K, 30 ml aqueous glycerol (10 wt%), catalyst (1 g), N_2 (0.1 MPa), 1 h. [b] Total yield of liquid products. [c] C-based composition of liquid products/mol%.

In addition, the effect of glycerol concentration and the amount of catalyst on the glycerol reaction over Raney Ni catalyst was also investigated. Higher conversion was obtained at lower glycerol concentrations. 100% glycerol conversion and 58.5% yield of total liquid products could be obtained when a 10% aqueous solution of glycerol was used (see Table S1, ESI).† Taking into consideration actual application, all the experiments were carried out using 10% glycerol concentration. The glycerol conversion was markedly enhanced by increasing the amount of the catalyst; however, the total yield of the liquid products decreased, which indicated that further C–C cleavage happened (see Table S2, ESI).† It is necessary to optimize the amount of catalyst to obtain the highest yield of diols. Besides, the catalyst showed good stability because it could be easily recovered after reaction and reused three times without any significant loss of its activity.

To further elucidate the reaction processes, PG and EG were also used as the reactants (see Table 3). Indeed, further C–C cleavage and C–O cleavage could happen under the reaction conditions. Combining the gas-phase product (only CH_4 and CO_2 were detected by GC), the possible reaction process could be proposed as the following (Scheme 2): firstly, aqueous glycerol reforming reaction happened to form CO_2 and active H atoms that were produced *in situ* on the Raney Ni catalyst, and the active H atoms were expected to show high hydrogenolysis activity; secondly, hydrogenolysis of glycerol to PG and EG with active H atoms over Raney Ni happened. During the reaction



Scheme 2 Proposed reaction pathway under the reaction conditions.

course, further degradation of diols and methanation were the main side reactions.

In conclusion, a new and efficient catalytic route for the production of PG and EG by catalytic combination of glycerol aqueous reforming and hydrogenation of glycerol has been developed using the commercial Raney Ni as catalyst. The new route provides a feasible approach for the direct use of a by-product of bio-diesel, facilitating an energy-efficient and atom-economic process. This process can be commercialized easily according to the following considerations. Firstly, the reaction conditions are much milder than those previously reported, since no hydrogen was needed and the reaction can be conducted under ambient pressure and the diluted aqueous glycerol can be directly used as the substrate without any concentration. Secondly, the catalyst is the commonly used commercial Raney Ni which is remarkably cheaper than the noble metal catalysts. It is interesting to find that the Raney Ni can be easily recovered from the reaction mixture by filtration or magnetic separation since Raney Ni is paramagnetic, and the catalyst can be conveniently reused without any further treatment. Thirdly, the two diol products can be easily separated from the reaction system because glycerol is totally converted and the catalyst can be easily removed. Finally, the gaseous products are very useful since they are mixture of CH_4 and CO_2, no CO was detected, which is very convenient for its further use as fuel or a hydrogen resource.

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