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One-pot synthesis of propylene glycol and dipropylene glycol over strong basic catalyst

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1. Introduction

Solid base catalysts play a decisive role in a large number of reactions essentially for fine chemical synthesis. Compared to homogeneous catalysts, which lead to the problems of products separation and catalysts recycle, solid base catalysts are noncorrosive and present fewer disposal problems, and they allow both easier separation and recovery of the products, catalysts, and solvent. Therefore, solid base catalysts are expected to offer environmentally benign and more economical pathways for the synthesis of fine chemicals, which have attracted much attention in recent years [1–8]. In the present work, several solid base catalysts, especially Na₂O–ZrO₂, which had been used in our laboratory in the synthesis of both dimethyl carbonate (DMC) and propylene glycol methyl ether (PGME) [9–11], were investigated for the propylene oxide hydrolysis.

As known, propylene glycol (PG), which can be used as unsaturated polyester resins, surface coating, non-ionic detergent and antifreeze, is the main product in the hydrolysis of propylene oxide. The technical-grade PG is prepared by catalytic hydration of propylene oxide with sulfuric acid as catalyst, which corrodes the equipments and pollutes the environment. The production is also carried out by non-catalytic hydration using a great deal of water as one of the reactants, which greatly increase the energy expenditure of product separation [12]. This is the same for the production of dipropylene glycol (DPG) [13]. Actually, the produc-



The synthesis of propylene glycol (PG) and dipropylene glycol (DPG) was carried out by the hydrolysis of propylene oxide over solid base catalysts. Among them, sol-gel derived Na_2O -ZrO₂ showed the excellent performance. It was found that Na_2O -ZrO₂ had a mesoporous framework in which Na_2O nanoparticles were homogeneously dispersed. Such a structure led to the strong basicity and then the excellent performance in the hydrolysis of propylene oxide. As a result, one-pot synthesis of propylene glycol (PG) and dipropylene glycol (DPG) could take place at a low H_2O/PO ratio of 3 without any condensation reactions. Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.

tion of PG can also be conducted by taking base as the catalyst, but it was hardly reported. Herein the synthesis of PG and DPG were carried out with solid base catalysts. This provides an effective and facile route for the synthesis of PG and DPG at a low H_2O/PO ratio of 3 and mild condition.

2. Experimental

2.1. Catalyst preparation

Typically, 1 g of amphiphilicpoly (alkyleneoxide) blockcopolymers PEO₂₀PPO₇₀PEO₂₀, Pluronic P123) was dissolved in a designed amount of absolute ethanol to form solution A. At the same time, 4.45 g of zirconium(IV) n-propoxide (23-28% free alcohol, Strem Chemicals) were mixed with 0.5 g of acetylactone (acac) under stirring to form solution B, in which acetylactone acted as a stabilizer to prevent the zirconium(IV) *n*-proposide from uncontrollable hydrolysis in the following step. Afterwards, solution B was slowly added to solution A under vigorous stirring. Upon stirring at room temperature for 1 h, 1.8 g of deionized water was added dropwise. The mixture, with molar ratio of 1 Zr:0.02 P-123:0.5 acac:80 EtOH:10 H₂O, was gelled in a closed vessel at 40-60 °C for 24 h. The obtained transparent resin hybrid was smashed and partly refluxed in a Teflon vessel that contained aqueous solution of $0.25-1.0 \text{ mol } \text{L}^{-1}$ NaOH for another 24 h. Then, the suspension was filtering without wash to remove the free Na⁺ in the solution. For the removal of the surfactant species, finally, the samples were heated in flowing N₂ at a rate of 1 °C min⁻¹ to 700 °C. The products were denoted as xNa_2O-ZrO_2 , herein x stands for the mass fraction



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of Na in Na₂O–ZrO₂. ZrO₂, MgO–ZrO₂ and CaO–ZrO₂ were synthesized following the literatures [14,15].

2.2. Characterization

The materials were characterized by a Rigaku D/max-A X-ray diffractometer (XRD) with $\lambda = 0.1541$ nm, Cu K α radiation in the 2θ range of 10–90° with the step of 0.02° at room temperature. Their specific surface areas were measured with a Tristar 3000 analyzer using the multipoint Brunauer, Emmett and Teller (BET) adsorption. Powder X-ray diffraction (XRD) experiments were carried out on a Rigaku Miniflex diffractometer using a Cu target with a Ni filter in a 2θ range of 10–80°. And the X-ray gun was operated at 50 kV and 30 mA, using a scan speed rate of 0.2°/min. The total basicity and base strength of the samples were measured by CO₂-TPD. About 0.1 g of sample were heated in flowing Ar (99.99%) at a rate of 5 °C min⁻¹ to 700 °C and kept at 700 °C for 1 h. When the temperature elevated, the CO₂ desorbed was detected by a Balza Q-Mass spectrometer.

2.3. Catalytic test

The catalytic performance of so-produced solid base was evaluated in the synthesis of propylene glycol and dipropylene glycol from propylene oxide and H₂O. The reaction was carried out in a stainless steel autoclave reactor with an inner volume of 150 ml. The standard procedure is as follows: 5.80 g of propylene oxide (PO), 5.40 g of distilled water and a certain amount of catalyst were introduced into the autoclave. The reaction was carried out at 90– 130 °C for 1–4 h under autogeneous pressure, and the autoclave was heated and magnetically stirred constantly during the reaction. Moreover, other 3 heterogeneous bases were used as references. The products were analyzed by a gas chromatograph (GC-



Fig. 1. Nitrogen adsorption–desorption isotherm of $Na_2O\text{-}ZrO_2$ with different sodium content.

920, Shanghai Haixin Chromatograph Instrument Co. Ltd.) with a flame ionization detector and a HP-5 column after filtration from the catalyst. The selectivity was defined as $m_i/\sum m_i \times 100$, where m_i was the molar of product of i, and $\sum m_i$ was the total molars of the products.

3. Results and discussion

3.1. Textural structure and phase

The porosity of Na₂O–ZrO₂ solid bases with different sodium contents were determined by N₂ adsorption–desorption technique. As shown in Fig. 1, their N₂ adsorption–desorption isotherms displayed type IV isotherms with clear hysteresis loops associated with capillary condensation, indicating the existence of mesoporous framework. Furthermore, BET surface area of those samples gradually decreased with the Na content. It was also found that with the Na content increased, the type IV adsorption isotherms became unconspicuous (see Table 1). This suggested the increase of Na content had a negative effect on the mesoporous framework of Na₂O–ZrO₂ solid bases.

Fig. 2 illustrates the wide-angle XRD patterns of Na_2O -ZrO₂ with different sodium content. It could be seen that only the diffraction peak of tetragonal zirconia was observed for the catalyst with the Na content of 0.05–0.20. Soler-Illia and Ozin [16,17] found that the presence of hetero-atom such as Si and Y in the ZrO₂ skeleton could reduce the contraction of the mesoporous zirconia. In the present case, the introduction of Na element into ZrO₂ might stabilize the tetragonal zirconia and then Na₂O nanoparticles might be homogeneously dispersed in the mesoporous zirconia framework at the Na content of 0.05–0.20. As a result, the structure of Na₂O–ZrO₂ solid bases was greatly influenced by their composition.

3.2. Basicity

The basic strength and basicity of different solid basic catalysts were estimated by CO₂-TPD (see Fig. 3). Except ZrO₂, two distinct desorption peaks were observed for other samples, indicating two kinds of basic sites with different basic intensity present on their surface. Among them, the peak at 120 °C could be contributed to the weak basic site of zirconia [18]. CaO–ZrO₂ showed the strong basic sites due to a sharp desorption peak at 600 °C, while MgO– ZrO₂ had the moderate strength basic sites with a sharp desorption peak at 300 °C. Mesoporous Na₂O–ZrO₂ showed the strongest basicity with the peak at 700 °C. During the sol–gel process, zirconium alkoxide and the template formed the gel after ageing, and Na₂O was incorporated into the ZrO₂ surface. However, they were too tiny to be detected by XRD (see Fig. 2). Thus, those highly-dispersed Na₂O gave rise to the high basicity.

Table 1

The surface area, porous channel structure and CO_2 uptake of Na_2O -Zr O_2 solid bases.

Samples	$S_{\text{BET}} (m^2 g^{-1})$	D _{BJH} (nm)	$V p (cm^3 g^{-1})$	CO ₂ uptake	CO ₂ uptake	
				(µ mol/g)	$(\mu \text{ mol}/m^2)$	
0.05 Na ₂ O-ZrO ₂	168.2	3.2	0.2	101.3	0.6	
0.10 Na ₂ O-ZrO ₂	151.3	6.2	0.3	171.3	1.1	
0.15 Na ₂ O-ZrO ₂	105.0	7.4	0.3	244.0	2.3	
0.2 Na ₂ O-ZrO ₂	86.6	5.6	0.2	268.7	3.1	

xNa₂O-ZrO₂, herein x stands for the mass fraction of Na in Na₂O-ZrO₂.



Fig. 2. XRD patterns of Na₂O-ZrO₂ with different sodium contents.



Fig. 3. CO2-TPD profiles of different solid bases.

Table 2	
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Samples	PO conversion (%)	Selectivi	Selectivity (%)		
		PG	DPG	TPG	
ZrO ₂	5.1	100	0	0	
MgO-ZrO ₂	10.2	100	0	0	
CaO-ZrO ₂	23.2	94.8	5.2	0	
Na ₂ O-ZrO ₂	99.9	46.2	41.3	12.5	

Reaction condition: propylene oxide 5.8 g, deionized water 5.4 g, cat 0.3 g, 2 h, 100 $^\circ\text{C}.$

3.3. Catalytic performance

Table 2 gives the catalytic performance of solid bases in the hydrolysis of propylene oxide. The main products were propylene glycol (PG), dipropylene glycol (DPG) and tripropylene glycol (TPG). Among different solid bases, as-prepared mesoporous Na₂O–ZrO₂ had a remarkably activity. Compared with MgO–ZrO₂ and CaO–ZrO₂, Na₂O–ZrO₂ showed the high PO conversion of 99.9%. This could be attributed to the higher charge density of O^{2-} with Na⁺ than that of O^{2-} with Mg²⁺ or Ca²⁺, which gave rise to the increase in the basic strength (see Fig. 3). Taking the advantages of both mesoporous structure and super strong base, Na₂O–ZrO₂ showed the best performance in the reaction among the catalysts.

In general, PG could be synthesized by PO and water, and then PG and PO reacted into DPG. Afterwards, TPG was produced by PO and DPG. During these reactions, no PG or DPG self-condensation were observed. As a result, the sodium contents had a great influence on the PO conversion (see Fig. 4). The conversion of PO increased with the Na content, which was due to the improvement of basicity by the sodium. The conversion reached almost 90% for 0.20 Na₂O–ZrO₂, but 0.05 Na₂O–ZrO₂ only gained no more than 40% at 30 min. In any case, the PO conversion finally reached almost 100% at 4 h.

Moreover, the reaction parameters also showed the different effect on both PO conversion and product selectivity with $0.10 \text{ Na}_2\text{O}_2\text{ rO}_2$ as the catalyst (see Fig. 5(a–d)). With the reaction in the temperature region from 90 to 130 °C, the selectivity of DPG decreased a little with the temperature (see Fig. 5(a)), since the reaction was an exothermic reaction with the higher thermodynamic equilibrium constant than PG. Furthermore, both PO conversion and selectivity almost had no change after 2 h (see Fig. 5(b)). This could be attributed to the 100% conversion of PO without any condensation reactions. Moreover, at the molar ratio of H₂O to PO over 3, the DPG selectivity sharply decreased, indicating that the excessive H₂O was favorable for the production of the incipient product PG (see Fig. 5(c)). In addition, the PO conversion increased a little at the amount of catalyst up to 2.0 wt% (see Fig. 5(d)), but the selectivity of DPG ascended with the increase of the amount of catalyst.



Fig. 4. The influence of different sodium contents of $Na_2O\text{-}ZrO_2$ on the PO conversion.



Fig. 5. (a-d) Effects of the reaction parameters.

4. Conclusion

 Na_2O-ZrO_2 , as a super basic solid catalyst, could be prepared via an appropriate sol-gel process. With such a catalyst, the synthesis of propylene glycol (PG) and dipropylene glycol (DPG) from the hydrolysis of propylene oxide (PO) could be carried out efficiently. Under the optimal reaction conditions, PO conversion, PG selectivity and DPG selectivity reached 99.9%, 46.2% and 41.3%, respectively. As a result, one-pot synthesis of PG and DPG could be conducted at a low H₂O/PO ratio without any condensation reactions.

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