Catalysis Communications 11 (2010) 675–678

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

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

Zhuo Liu [a,b], Wenbo Zhao [a], Fukui Xiao [a], Wei Wei [a,*], Yuhan Sun [a,*]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:
Received 3 April 2009
Received in revised form 4 January 2010
Accepted 7 January 2010
Available online 28 January 2010

Keywords:
Propylene glycol
Dipropylene glycol
Strong basic catalyst $Na_2O–ZrO_2$

ABSTRACT

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 $Na_2O–ZrO_2$ showed the excellent performance. It was found that $Na_2O–ZrO_2$ 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.

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 $Na_2O–ZrO_2$, 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 production 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 $PEO_{20}PPO_{70}PEO_{20}$, 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*–propoxide 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 H_2O, 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 $mol\ L^{-1}$ 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 N_2 at a rate of 1 °C min^{-1} to 700 °C. The products were denoted as $x Na_2O–ZrO_2$, herein *x* stands for the mass fraction

---

* Corresponding authors. Tel.: +86 351 4049612 (Y. Sun).
E-mail addresses: weiwei@sxicc.ac.cn (W. Wei), yhsun@sxicc.ac.cn (Y. Sun).

1566-7367/$ - see front matter Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2010.01.004

of Na in $Na_2O–ZrO_2$. ZrO_2, $MgO–ZrO_2$ and $CaO–ZrO_2$ 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 Kα 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 CO_2-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 CO_2 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 H_2O. 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-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.

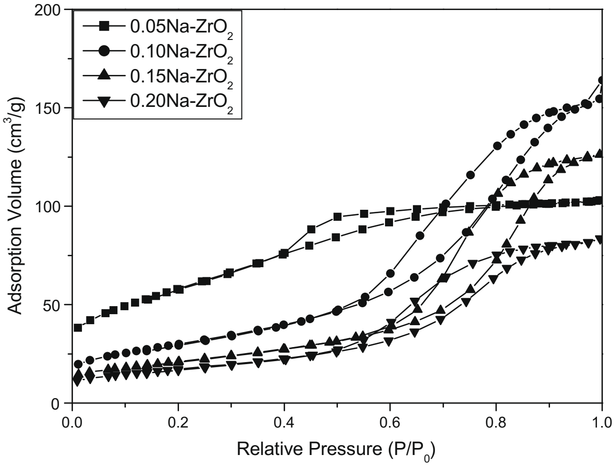

Fig. 1. Nitrogen adsorption–desorption isotherm of $Na_2O–ZrO_2$ with different sodium content.

3. Results and discussion

3.1. Textural structure and phase

The porosity of $Na_2O–ZrO_2$ solid bases with different sodium contents were determined by N_2 adsorption–desorption technique. As shown in Fig. 1, their N_2 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 $Na_2O–ZrO_2$ solid bases.

Fig. 2 illustrates the wide-angle XRD patterns of $Na_2O–ZrO_2$ 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 ZrO_2 skeleton could reduce the contraction of the mesostructure, which increased the structural stability of the mesoporous zirconia. In the present case, the introduction of Na element into ZrO_2 might stabilize the tetragonal zirconia and then Na_2O 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 $Na_2O–ZrO_2$ solid bases was greatly influenced by their composition.

3.2. Basicity

The basic strength and basicity of different solid basic catalysts were estimated by CO_2-TPD (see Fig. 3). Except ZrO_2, 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]. $CaO–ZrO_2$ showed the strong basic sites due to a sharp desorption peak at 600 °C, while $MgO–ZrO_2$ had the moderate strength basic sites with a sharp desorption peak at 300 °C. Mesoporous $Na_2O–ZrO_2$ 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 Na_2O was incorporated into the ZrO_2 and then partially inserted into the oxygen vacancy on the ZrO_2 surface. However, they were too tiny to be detected by XRD (see Fig. 2). Thus, those highly-dispersed Na_2O gave rise to the high basicity.

Table 1
The surface area, porous channel structure and CO_2 uptake of $Na_2O–ZrO_2$ solid bases.

Samples	S_{BET} ($m^2\ g^{-1}$)	D_{BJH} (nm)	Vp ($cm^3\ g^{-1}$)	CO_2 uptake	
				(μ mol/g)	(μ mol/m^2)
0.05 $Na_2O–ZrO_2$	168.2	3.2	0.2	101.3	0.6
0.10 $Na_2O–ZrO_2$	151.3	6.2	0.3	171.3	1.1
0.15 $Na_2O–ZrO_2$	105.0	7.4	0.3	244.0	2.3
0.2 $Na_2O–ZrO_2$	86.6	5.6	0.2	268.7	3.1

$xNa_2O–ZrO_2$, herein x stands for the mass fraction of Na in $Na_2O–ZrO_2$.