



## Short communication

## Zirconia-supported niobia catalyzed formation of propanol from 1,2-propanediol via dehydration and consecutive hydrogen transfer



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## ABSTRACT

Vapor-phase catalytic dehydration of 1,2-propanediol was investigated over Zirconia-supported niobia catalysts. The catalysts exhibit selectivity favoring propanol (approximately 39%) at 85.0% 1,2-propanediol conversion at 290 °C under 1 atm N<sub>2</sub>. The ZrNbO catalysts were analyzed by various techniques; the results indicated that the active sites were weak Brønsted acid sites. A dehydration and hydrogen transfer mechanism was also proposed.

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## 1. Introduction

Large amounts of glycerol are currently generated as a by-product in biodiesel manufacture by transesterification of seed oils [1]. The global production for refined glycerol has increased over the last few years at an average annual rate of 8.7%, and this increased supply has subsequently resulted in a sharp decrease in the price of this product [2]. Consequently, it is highly desirable to convert low-cost glycerol into value-added chemicals or materials. Toward this end, many research groups study transforming glycerol into value-added chemicals, such as dihydroxyacetone [3–5], acrolein [6,7], 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO) [8–11], and biopropanols, by catalytic processes.

Among the products, 1-propanol is also a high value commodity chemical, which is used mainly as a solvent, a component of printing ink and a chemical intermediate for the production of *n*-propyl acetate [12]. There are various strategies for the production of 1-propanol from glycerol or glycerol-derived PDO. One process used to access this compound involve the conversion of glycerol to biopropanols on using variety of catalysts [2,13]. Another well-developed procedure accesses biopropanols via glycerol-derived propanediols. So far, glycerol hydrogenolysis has been extensively studied. It has been known that the glycerol hydrogenolysis to 1,2-PDO is more selective than that to 1,3-PDO [14–17]. As a result, 1,2-PDO is more preferable as a substrate for the production of 1-propanol. On the other hand, there have been several works on the catalyst development for the glycerol hydrogenolysis to 1,3-PDO

like Rh–ReOx [18], Ir–ReOx [19], and Pt–WOx [20] and so on. Commonly, these catalysts showed the selective hydrogenolysis of 1,2-propanediol to 1-propanol (selectivity is beyond 80%) and that of 1,3-propanediol to 1-propanol [21]. Totally, the catalysts for the selective hydrogenolysis of glycerol to 1,3-propanediol have a potential in the production of 1-propanol from glycerol. However, these systems need high pressure hydrogen and Rh-based or Pt-based catalysts, which are expensive.

Achieving low cost and mild reaction conditions are the prime interests for this reaction. Zhang et al. [22] found zeolites can catalyze 1,2-PDO into 1-propanol at 250–300 °C at ambient pressure under nitrogen. However, as a by-product, the yield of 1-propanol was only 21.2%. Therefore, how to improve the 1-propanol yield from 1,2-PDO with a non-noble metal catalyst without using hydrogen is an interesting and challenging work.

Herein, we report the development of a ZrNbO catalyst; the use of this catalyst results in a 33.0% yield of 1-propanol at 85.0% conversion of 1,2-PDO under 1 atm N<sub>2</sub>. To the best of our knowledge, this is the highest yield of 1-propanol achieved under an inert atmosphere at ambient pressure. Notably, 1-propanol was formed as the main product, with acetol and propanal as additional products, even though no molecular hydrogen or additional hydrogen donor, such as 2-propanol [23] or formic acid, [24] was present in the system.

## 2. Experimental

## 2.1. Catalyst preparation

ZrO<sub>2</sub> ( $S_{\text{BET}} = 168 \text{ m}^2 \text{ g}^{-1}$ ) was prepared by the hydrolysis of zirconium chloride as reported by G.K. Chuah et al. [25].  $\gamma\text{-Al}_2\text{O}_3$

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**Table 1**  
Physico-chemical properties of the catalysts.

Catalyst	Nb (%)	Nb <sub>2</sub> O <sub>5</sub> (%)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Nb Surface density (Nb nm <sup>-2</sup> )
ZrO <sub>2</sub>	–	–	168	–
ZrNbO-0.7	1.6	2.37	153	0.7
ZrNbO-1.2	2.6	3.84	143	1.2
ZrNbO-2.0	4	5.94	131	2.0

(Chinalco, S<sub>BET</sub> = 500 m<sup>2</sup> g<sup>-1</sup>), and TiO<sub>2</sub> (P-25, Degussa, S<sub>BET</sub> = 55 m<sup>2</sup> g<sup>-1</sup>) were also tested for comparison.

30% HSiW/SiO<sub>2</sub> was prepared by an impregnation method, according to the literature [26]. 15% WO<sub>x</sub>/ZrO<sub>2</sub> was prepared by impregnation of zirconium oxyhydroxide solids with ammonium metatungstate solutions [27]. 15% WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and 15% WO<sub>x</sub>/TiO<sub>2</sub> were prepared by incipient wetness impregnation using ammonium metatungstate as the precursor. 5% NbO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> and 5% NbO<sub>x</sub>/TiO<sub>2</sub> were prepared by incipient wetness impregnation using ammonium oxalate-niobate as the precursor. All of above solution except HSiW/SiO<sub>2</sub> dried over night at 110 °C before grinding and calcination at 600 °C for 2 h.

ZrNbO catalyst was prepared by impregnation. The impregnation was conducted in acidified water with ammonium oxalate-niobate [6]. The samples obtained were denoted as ZrNbO-x, with x the Nb Surface density. It should be noted that support here is different from that in the work of P. Lauriol-Garbey et al. [6]. The support corresponds to a mixture of tetragonal and monoclinic phases with a specific surface area of 168 m<sup>2</sup> g<sup>-1</sup> (Table 1).

## 2.2. Catalyst characterization

The X-ray powder diffraction (XRD) patterns of catalyst samples were obtained with a Bruker D8 Advance X-ray diffraction meter under Ni-filtered Cu-Kα radiation. BET surface area was measured by nitrogen adsorption on a Micromeritics ASAP 2020 surface area and porosity analyzer. NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD experiments were performed with a Micromeritics Autochem II chemisorption analyzer. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded with a Nicolet 710 FT-IR spectrometer.

## 2.3. Catalytic test

The conversion of 1,2-PDO to 1-propanol was performed in a fixed-bed reactor (8 mm i.d.). In a typical reaction, 1 g of catalyst was mixed with a known amount of quartz sand and put into the tube reactor. After the temperature of the reactor had reached 290 °C, a 30 wt.% 1,2-PDO aqueous solution was pumped into the reactor at a flow rate of 1.8 mL h<sup>-1</sup> using a syringe pump (SSI Series II Pump). Nitrogen, at a flow rate of 30 mL min<sup>-1</sup>, was used as carrier gas. The products were collected hourly in ethanol cooled by an ice-water trap. The products in the resultant solutions were identified by data collected from gas chromatograph (GC, 7890A, Agilent, USA) coupled with a mass spectrometer (MS, 5975C, Agilent, USA) after the reaction was complete.

## 3. Results and discussion

The performance of different catalysts with respect to 1,2-propanediol conversion was tested, and the results were shown in Table 2. Over ZrO<sub>2</sub>, 1,2-propanediol was transformed mainly to acetol via dehydrogenation with 22.9% selectivity, propanal and acetone via dehydration and, finally, only 19.8% 1-propanol was detected (Table 2, entry 1). Over Al<sub>2</sub>O<sub>3</sub>, the selectivity for 1-propanol was only 17.4% (Table 2, entry 2) and 11.2% selectivity for 1-propanol over TiO<sub>2</sub> (Table 2, entry 3) was observed. However, the overall conversion of 1,2-propanediol was still low over these catalysts.

When using strongly Brønsted acidic 30% HSiW/SiO<sub>2</sub>, propanal was produced with a selectivity of 86.0% via pinacol rearrangement [28] (Table 2, entry 5). Nb<sub>2</sub>O<sub>5</sub>, which is strongly Lewis acidic (Aladdin, 99.95%), produced products in lower selectivity with

**Table 2**  
Results of 1,2-propanediol conversion over various catalysts<sup>a</sup>.

Entry	Catalyst	Conversion (%)	Yield <sup>b</sup> (%)	S <sub>i</sub> <sup>c</sup> (%)				
				Propanol	Propanal	Dioxolane	Acetol	Acetone
1	ZrO <sub>2</sub>	53.7	10.6	19.8	17.9	–	22.9	2.4
2	γ-Al <sub>2</sub> O <sub>3</sub>	36.3	6.3	17.4	18.6	6.7	33.4	3.5
3	TiO <sub>2</sub>	32.9	3.7	11.2	26.2	0.4	13.5	11.6
4	Nb <sub>2</sub> O <sub>5</sub>	94.8	9.2	9.7	51.2	5.1	3.3	12.7
5	30%HSiW/SiO <sub>2</sub> <sup>d</sup>	96.9	1.2	1.2	86.0	3.2	–	5.0
6	WO <sub>x</sub> /ZrO <sub>2</sub>	86.4	13.9	16.1	54.3	4.1	10.3	1.0
7	WO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	81.9	11.7	14.3	63.6	–	2.9	1.8
8	WO <sub>x</sub> /TiO <sub>2</sub>	82.0	2.0	2.8	66.6	1.0	4.1	10.4
9	NbO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	85.1	9.8	11.5	44.2	3.3	11.5	4.9
10	NbO <sub>x</sub> /TiO <sub>2</sub>	74.5	6.8	9.1	33.4	0.5	6.4	8.6
11	ZrNbO-0.7	70.9	19.1	27.0	25.0	–	15.1	3.6
12	ZrNbO-1.2	85.0	33.1	39.0	27.4	1.0	21.8	4.7
13	ZrNbO-2.0	86.1	26.2	30.5	29.7	–	18.9	9.5
14	Ferrierite(20) <sup>e</sup>	83.2	21.2	25.5	29.1	39.1	–	1.2

<sup>a</sup> Reaction conditions: temperature 290 °C, N<sub>2</sub> flow rate 30 mL min<sup>-1</sup>, 1,2-propanediol WHSV = 1.8 h<sup>-1</sup>, 1 g catalyst, conversion and selectivity were calculated by collecting the effluent produced between initial 1 and 8 h.

<sup>b</sup> Yield of propanol.

<sup>c</sup> S<sub>i</sub> = Carbon selectivity, dioxolane, 2-ethyl-4-methyl-1,3-dioxane; other by-products are allyl alcohol, 2-ethyl-2-butenal, 2-methyl-2-cyclopenten-1-one, acetic acid and several unknown products.

<sup>d</sup> T = 210 °C.

<sup>e</sup> Reference [12]

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