



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 N₂. 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 N₂. 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

ZrO₂ ($S_{\text{BET}} = 168 \text{ m}^2 \text{ g}^{-1}$) 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 ₂ O ₅ (%)	S _{BET} (m ² g ⁻¹)	Nb Surface density (Nb nm ⁻²)
ZrO ₂	–	–	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_{BET} = 500 m² g⁻¹), and TiO₂ (P-25, Degussa, S_{BET} = 55 m² g⁻¹) were also tested for comparison.

30% HSiW/SiO₂ was prepared by an impregnation method, according to the literature [26]. 15% WO_x/ZrO₂ was prepared by impregnation of zirconium oxyhydroxide solids with ammonium metatungstate solutions [27]. 15% WO_x/Al₂O₃ and 15% WO_x/TiO₂ were prepared by incipient wetness impregnation using ammonium metatungstate as the precursor. 5% NbO_x/Al₂O₃ and 5% NbO_x/TiO₂ were prepared by incipient wetness impregnation using ammonium oxalate-niobate as the precursor. All of above solution except HSiW/SiO₂ 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 m² g⁻¹ (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. NH₃-TPD and CO₂-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⁻¹ using a syringe pump (SSI Series II Pump). Nitrogen, at a flow rate of 30 mL min⁻¹, 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 ZrO₂, 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 Al₂O₃, the selectivity for 1-propanol was only 17.4% (Table 2, entry 2) and 11.2% selectivity for 1-propanol over TiO₂ (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/SiO₂, propanal was produced with a selectivity of 86.0% via pinacol rearrangement [28] (Table 2, entry 5). Nb₂O₅, 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^a.

Entry	Catalyst	Conversion (%)	Yield ^b (%)	S _i ^c (%)				
				Propanol	Propanal	Dioxolane	Acetol	Acetone
1	ZrO ₂	53.7	10.6	19.8	17.9	–	22.9	2.4
2	γ-Al ₂ O ₃	36.3	6.3	17.4	18.6	6.7	33.4	3.5
3	TiO ₂	32.9	3.7	11.2	26.2	0.4	13.5	11.6
4	Nb ₂ O ₅	94.8	9.2	9.7	51.2	5.1	3.3	12.7
5	30%HSiW/SiO ₂ ^d	96.9	1.2	1.2	86.0	3.2	–	5.0
6	WO _x /ZrO ₂	86.4	13.9	16.1	54.3	4.1	10.3	1.0
7	WO _x /Al ₂ O ₃	81.9	11.7	14.3	63.6	–	2.9	1.8
8	WO _x /TiO ₂	82.0	2.0	2.8	66.6	1.0	4.1	10.4
9	NbO _x /Al ₂ O ₃	85.1	9.8	11.5	44.2	3.3	11.5	4.9
10	NbO _x /TiO ₂	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) ^e	83.2	21.2	25.5	29.1	39.1	–	1.2

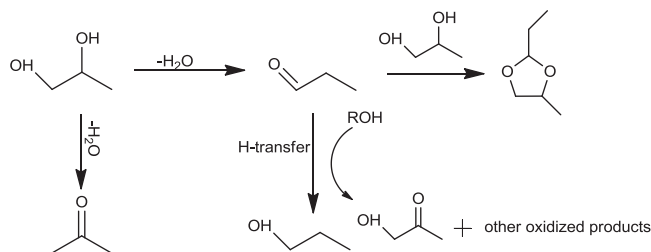
^a Reaction conditions: temperature 290 °C, N₂ flow rate 30 mL min⁻¹, 1,2-propanediol WHSV = 1.8 h⁻¹, 1 g catalyst, conversion and selectivity were calculated by collecting the effluent produced between initial 1 and 8 h.

^b Yield of propanol.

^c S_i = 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.

^d T = 210 °C.

^e Reference [12]



Scheme 1. Reaction pathways from 1,2-propanediol to propanol.

respect to propanal (51.2%, Table 2, entry 4). A series of supported tungsten oxide catalysts, with strong, medium strong and weak acid sites [29], produced propanal as the principal product and some 1-propanol could also be detected over WO_x/ZrO_2 and $\text{WO}_x/\text{Al}_2\text{O}_3$, but not WO_x/TiO_2 (Table 2, entries 6–8). $\text{NbO}_x/\gamma\text{-Al}_2\text{O}_3$ produced more propanal, with a selectivity of 44.2%, than $\text{NbO}_x/\text{TiO}_2$ (33.4%) (Table 2, entries 9, 10), but the yield of the desired 1-propanol was still relatively low (<10%). Unexpectedly, ZrNbO catalysts gave a remarkable increase in the yield of 1-propanol (Table 2, 11–13). The yield of 1-propanol was dramatically improved when the content of Nb was increased to 1.2 atom nm^{-2} . 2. ZrNbO-1.2 showed the highest 1-propanol yield of 33.1%, however, further increase of Nb density led to the decrease of 1-propanol yield.

Zhang et al. [22] proposed that both the formation of 1-propanol and the formation of dioxolane were linked to the same properties of catalyst. Bergman et al. recently reported the preparation of allyl alcohol via a formic acid-mediated deoxygenation of glycerol [24]. Obviously, our catalytic results cannot be explained based solely on the above results because very little dioxolane was found and no formic acid was present in our experiments. Schüth et al. inferred that glycerol was converted to allyl alcohol through dehydration and consecutive hydrogen

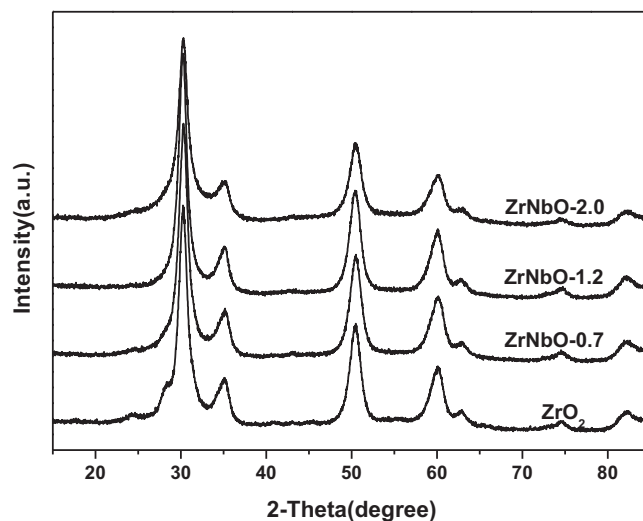


Fig. 1. Powder X-ray diffraction patterns of the catalysts.

transfer [30]. This explanation better suits our system and the probable reaction pathway is shown in Scheme 1.

Acetone and propanal are both products of the 1,2-propanediol dehydration reaction and dioxolane is produced from the reaction between the 1,2-propanediol and propanal. 1-Propanol may be obtained through a hydrogen transfer reaction with an alcohol acting as the hydrogen donor. It is worth noting that selectivity for acetol was lower than that of 1-propanol, indicating that 1,2-propanediol may not be the only the hydrogen donor for the hydrogen transfer reaction. According to previous literature reports [30], some intermediates with hydroxyl groups were formed during reaction, resulting in a mixture of these products

Table 3

Yields of hydrogen transfer reactions between propanal and different alcohols catalyzed by ZrNbO catalysts^a.

Entry	Substrate	H-donor	Product	Conv ^b (%)	Conv ^c (%)	Yield ^d (%)	S ^e (%)
1				85.0	87.5	2.7	3.2
2				88.2	84.3	3.2	3.6
3				93.3	85.3	4.3	4.8
4				87.5	77.8	4.8	5.5
5				92.4	90.5	1.4	1.5
6				85.6	82.1	3.9	4.6
7 ^f				94.5	86.4	15.7	16.7

^a All yields are based on GC results with quantification. Propanal was premixed with the corresponding alcohol at a molar ratio of 1:1 and then pumped through the reactor at the same temperature, catalyst amount, and flow rate.

^b The conversion of substrate.

^c The conversion of H-donor.

^d The yield of products based on substrate.

^e Selectivity of 1-propanol.

^f 1,2-propanediol: propanal molar ratio=2:1, propanol yield was calculated based on the amount of 1,2-propanediol.

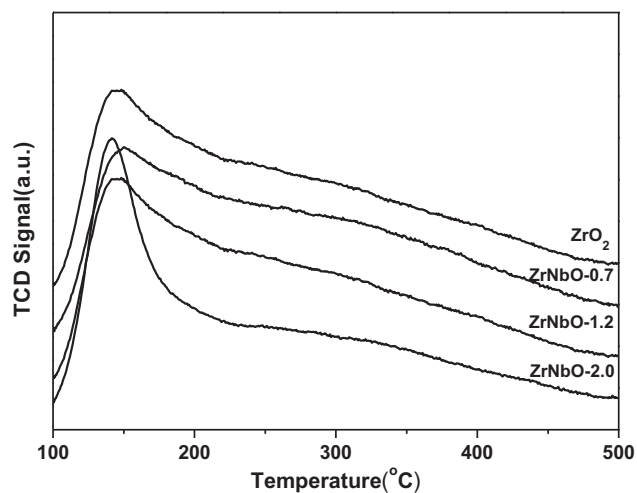


Fig. 2. NH₃-TPD profiles of the ZrNbO catalyst species.

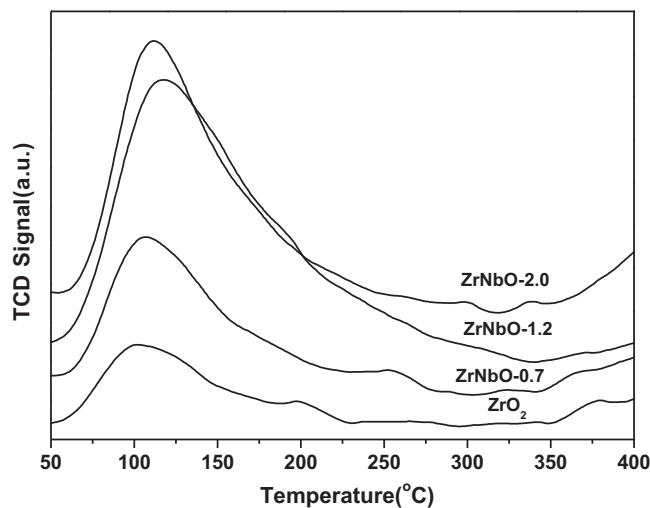


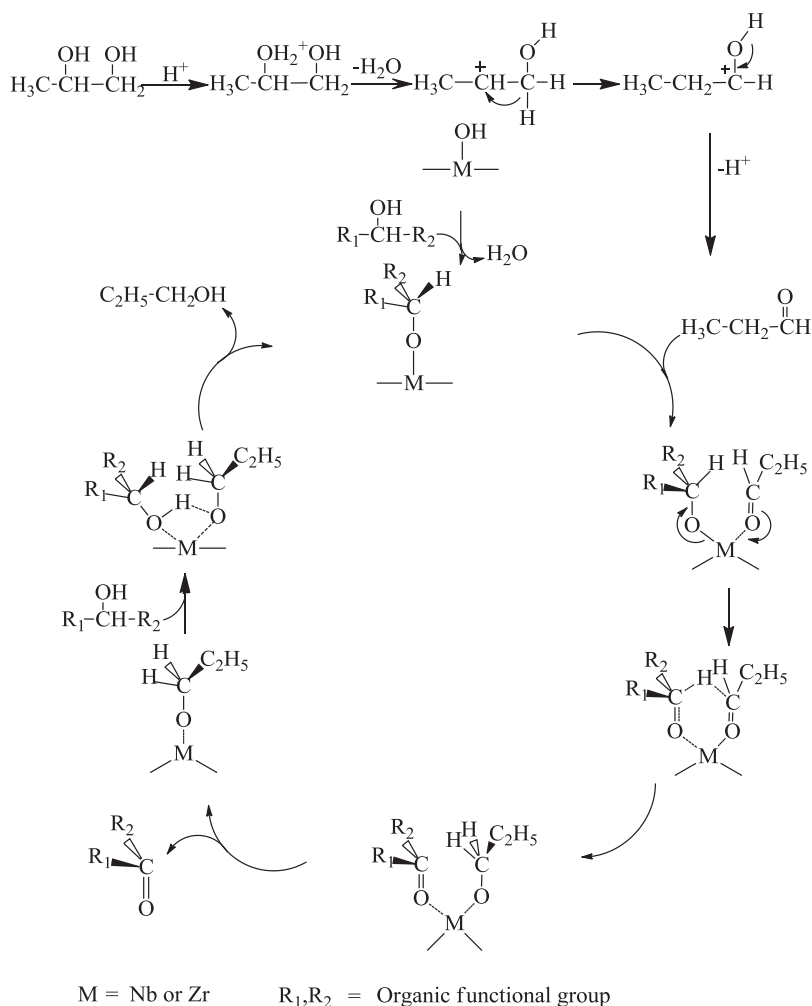
Fig. 3. CO₂-TPD profiles of the ZrNbO catalyst species.

with 1,2-propanediol; any of these compounds could then serve as the hydrogen donor.

To better understand the mechanism, several reactions between different alcohols and propanal were performed, and the results are shown in Table 3. It can be seen that hydrogen transfer reactions can indeed take place with a variety of alcohols,

although the yields of the 1-propanol are considerably lower than for the ZrNbO–1,2-propanediol system. These results confirmed that the hydrogen transfer does not only include the reaction between 1,2-propanediol and propanal.

To understand the origin of the observed catalytic properties, studies on the structure and surface formation of ZrNbO catalyst



Scheme 2. Possible mechanism of 1,2-propanediol converted to propanol over ZrNbO catalysts.

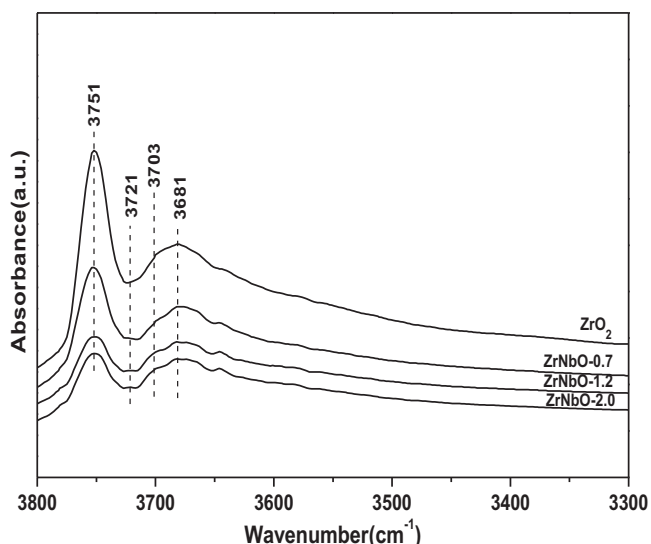


Fig. 4. In situ DRIFTS spectra of the hydroxyl region of supported niobia catalysts.

samples were conducted. The X-ray diffraction pattern of ZrO₂ revealed two phase, which corresponded to tetragonal zirconia (t-ZrO₂) and monoclinic zirconia (m-ZrO₂) (Fig. 1). The relative m-ZrO₂ phase disappeared when niobium was incorporated into ZrO₂. It means that niobium helps in the stabilization of the tetragonal form [6] (Fig. 1). The TPD of NH₃ and CO₂ were also measured to investigate the surface acid-base properties of the catalysts. Fig. 2 showed NH₃-TPD profiles of the ZrNbO samples. All of the thermograms have two broad maxima: the first of these was found at approximately 150 °C, and the second occurred in the range between 300 and 400 °C. For the ZrNbO samples, the density of the weak acid sites increased with increasing the Nb content while the density of the strong acid sites decreased accordingly. Fig. 3 shows TPD profiles of CO₂ adsorbed on ZrNbO catalysts. CO₂ was desorbed in a wide temperature range. The peak intensities in TPD profiles of CO₂ increased gradually as the Nb content increased. This indicated that ZrO₂ had weak basicity and the surface basicity were enhanced by the addition of Nb. Fig. 4 shows in situ DRIFTS spectroscopy results for different samples. The hydroxyl region of zirconia displayed two bands at 3681 and 3751 cm⁻¹, which have been assigned to surface hydroxyl groups bonded to three and one Zr atoms, respectively [31]. The larger decrease in intensity of the band at 3751 cm⁻¹ indicated that hydroxyl groups bound to a single Zr atom were more reactive toward deposited niobia [31]. The new band at 3721 cm⁻¹ and the shoulder at 3703 cm⁻¹, for both of which the assignments were unknown, may be due to isolated Nb–OH hydroxyl groups or Nb–OH–Zr bridging hydroxyl groups [32].

In the ZrNbO catalysts, Brønsted acid sites are the active sites for the dehydration reaction [6,33]. The Brønsted acid sites have also been shown to be active in and selective for the Meerwein–Ponndorf–Verley reduction [34,35]. Based on the above results, the 1-propanol formation mechanism catalyzed by ZrNbO catalysts can be proposed as follows (Scheme 2). A reaction mechanism for the conversion of 1,2-propanediol to propanal has already been proposed for zeolites [22]. We propose that the weak Brønsted acid sites act as sites for ligand exchange with the alcohol (1,2-propanediol and some intermediates with hydroxyl groups) to form alkoxides on the catalyst. Propanal coordinates to the

Brønsted acid sites, activating the carbonyl group and initiating a hydride transfer from alcohol to the carbonyl. A ketone is formed and subsequent alcoholysis leads to the product, 1-propanol, and regeneration of the active catalyst.

4. Conclusions

In summary, a process for the conversion of 1,2-propanediol to 1-propanol over a ZrNbO catalyst was reported. A dehydration and hydrogen transfer mechanism was proposed. The ZrNbO species are active and selective catalysts for this reaction. The weak Brønsted acid sites may play a crucial role in the conversion of 1,2-propanediol to 1-propanol.

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