Aqueous-phase deoxygenation of glycerol to 1,3-propanediol over $Pt/WO_3/ZrO_2$ catalysts in a fixed-bed reactor

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Deoxygenation of glycerol in aqueous medium catalyzed by $Pt/WO_3/ZrO_2$ at relatively low temperatures (110–140 °C) under hydrogen pressure range from 2 to 5 MPa in a fixed-bed continuous-flow reactor gives 1,3-propanediol (1,3-PDO) and *n*-propanol (*n*-PrOH) as the predominant products, indicating high selectivity for deoxygenation of the secondary hydroxyl group over the primary hydroxyl groups of the glycerol. The optimum catalyst was prepared by calcination of WO_3/ZrO_2 at 700 °C and loading of 3.0 wt% Pt with W content of 10 wt%. The effect of reaction temperature, hydrogen pressure and initial water content were evaluated to find the optimum reaction conditions. The glycerol conversion and the yield of 1,3-PDO greatly depended on these factors. At 130 °C, 4 MPa and 70.2% conversion, the yield of 1,3-PDO was up to 32.0% (1,3-PDO/1,2-PDO = 17.7). The proposed mechanism for glycerol deoxygenation in aqueous medium over $Pt/WO_3/ZrO_2$ is an ionic pathway involving proton and hydride ion transfer steps.

1. Introduction

Production of chemicals by catalytic transformation of bio-sustainable resources is a global challenge.[1] Recent development of biodiesel production by transesterification of plant oils and animal fat has made a large amount of glycerol available as a renewable feedstock for the synthesis of a wide range of value-added chemicals.[2–5] Significant research effort has been focused on the conversion of glycerol by catalytic processes such as reforming, oxidation, dehydration, esterification, etherification, deoxygenation and so on.[1–6] Synthesis of 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO) from glycerol *via* catalytic deoxygenation has attracted significant interest.[7–17] 1,2-PDO is an important commodity chemical, which finds use as antifreeze, aircraft de-icer, and as a component of coating and lubricant. 1,3-PDO is more valuable than 1,2-PDO, in particular, as a raw material for the production of polyesters. Significant advances have been made into the deoxygenation of glycerol to 1,2-PDO by using heterogeneous catalysts.[8,16] In contrast, the conversion of glycerol to 1,3-PDO is still a challenge. Relatively well developed is the fermentation process using bacterial strains in which glycerol is converted to 1,3-PDO. However, the fermentation process has some drawbacks. One of the main drawbacks is its low theoretical yield, owing to the byproducts, such as ethanol, acetate, lactate, butyrate and CO_2 formed in this process. Another main drawback is that the process is substrate inhibited. The bacteria used in the fermentation are generally not able to stand a glycerol concentration above 17%. As a result, both the product concentration and the productivity are low.[18] Hawley and co-workers[19] have carried out a selective dehydroxylation of glycerol to 1,3-PDO in three steps, but despite a high selectivity for 1,3-PDO (>70%) the reaction sequence was rather complicated and required the stoichiometric use of tosyl chloride.

There have been several reports on homogeneous and heterogeneous catalysts for the catalytic deoxygenation of glycerol to 1,3-PDO. Che[20] developed the catalytic deoxygenation of glycerol in 1-methyl-2-pyrolidinone under 32 MPa syngas at 200 °C and in the presence of a homogeneous rhodium complexes catalyst $Rh(CO)_2(acac)$ and H_2WO_4. Through the process, 1,3-PDO and 1,2-PDO were produced with 21% and 23% yield, respectively. Bullock and co-workers[21,22] described the deoxygenation of glycerol catalyzed by a homogeneous ruthenium complex in sulfolane under 5.2 MPa and 110 °C. The yield of 1,3-PDO was less than 5%. Chaminand *et al.*[7] reported a method for the production of 1,3-PDO using a catalyst system containing Rh/C and H_2WO_4 with discontinuous operation, achieving a 4% yield at 180 °C and 8.0 MPa. The highest 1,3-PDO/1,2-PDO ratio was 2.0 obtained in sulfolane. Kurosaka *et al.*[12] reported the deoxygenation of glycerol in 1,3-dimethyl-2-imidazolidinone at 170 °C and 8.0 MPa with discontinuous operation, in which the yields of 1,3-PDO was 24% over $Pt/WO_3/ZrO_2$ catalysts. The 1,3-PDO/1,2-PDO ratio was about 2.0. Tomishige and co-workers[11,23,24] reported the deoxygenation of glycerol in water at 120 °C and 8.0 MPa with discontinuous operation, in which the 1,3-PDO/1,2-PDO ratio was less than 0.7 over Rh/SiO_2 and modified Rh/SiO_2 catalysts.

Huang *et al.*[25] reported conversion of glycerol into 1,3-propanediol over $Cu–H_4SiW_{12}O_{40}/SiO_2$ in vapor phase without employing organic solvent. Through the process, 1,3-PDO and 1,2-PDO were produced with 32.1% and 22.2% selectivity, respectively. For high reaction temperature (210 °C), a lot of

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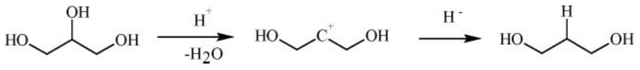
unknown products were produced. Since the evaporation of glycerol is energy-consuming, the liquid phase catalytic process will be more suitable.

However, there are several drawbacks in the previous attempts. The greatest drawback is the reaction medium. Regardless of catalyst type, 1,2-PDO is the predominant product and the selectivity to 1,3-PDO is lower in aqueous phase.[7–17,23,24] Chaminand *et al.*[7] found that the deoxygenation of glycerol to 1,3-PDO is favorable in polar aprotic solvent, thus most of the previous studies have been performed in high boiling-point organic solvent, *e.g.*, sulfolane ,[11,20,21] 1-methyl-2-pyrolidinone ,[20] 1,3-dimethyl-2-imidazolidinone.[12] It is well understood that this drawback will greatly reduce the environmental and economical viability. Another drawback is the slurry reactor, which presents difficulties in terms of catalyst separation from the reaction mixture.

The deoxygenation of glycerol to 1,3-PDO is a substitution reaction, in which a H atom substitutes for the secondary hydroxyl group in glycerol. As shown in eqn (1), one approach to selective deoxygenation of the secondary hydroxyl group of glycerol is sequential treatment with H^+ and H^- sources, releasing water and formally resulting in the conversion of OH to H.[20,21] Achieving catalytic deoxygenation of glycerol would require that proton and hydride transfer steps occur, followed by catalyst regeneration through heterolytic activation of H_2 to H^+ and H^-. A catalyst capable of heterolytic cleavage of H_2 could potentially enable use of H_2 as the source of both H^+ and H^-. Bullock and co-workers[20,21] described the deoxygenation of glycerol catalyzed by a homogeneous ruthenium complex in sulfolane through an ionic pathway involving proton and hydride transfer steps. But the yield of 1,3-PDO was less than 5%.



(1)

The $Pt/WO_3/ZrO_2$ and its modified version are efficient catalysts for skeletal isomerization of alkanes.[26–29] On $Pt/WO_3/ZrO_2$ catalyst, hydrogen molecules can be activated into protons and hydride ions *via* heterolytic cleavage at lower temperature.[30,31] Kurosaka *et al.*[12] reported the deoxygenation of glycerol in 1,3-dimethyl-2-imidazolidinone at 170 °C and 8.0 MPa over $Pt/WO_3/ZrO_2$ catalysts with discontinuous operation.

Considering water is a by-product of the glycerol deoxygenation, safe, inexpensive water is an ideal solvent. In order to avoid the evaporation of water and aqueous phase reforming of glycerol, we investigated $Pt/WO_3/ZrO_2$ as catalyst for glycerol deoxygenation in the aqueous phase in a fixed-bed continuous-flow reactor at low temperatures of 110–140 °C and hydrogen pressures of 2–5 MPa. Details of $Pt/WO_3/ZrO_2$ catalysts and the optimal reaction parameters were also investigated to improve the selectivity of the reaction towards 1,3-PDO. We will also discuss the formation routes of deoxygenation and consecutive deoxygenation products based on the catalytic performance when the products in the glycerol reaction were used as reactants.

2. Experimental

A series of WO_3/ZrO_2 samples with different tungsten contents were prepared by methods previously reported.[27,28] $Zr(OH)_4$ was obtained by hydrolysis of zirconium nitrate (99%, SCRC) solution with the addition of aqueous ammonium hydroxide (25–28%, SCRC) solution up to pH 9. The precipitate obtained was filtered, washed with de-ionized water and dried at 110 °C overnight. The dried $Zr(OH)_4$ was impregnated with the pre-calculated amount aqueous solution of ammonium metatungstate (99.999%, Acros Organics), the water was evaporated, and the samples were dried overnight at 110 °C. To investigate the effect of calcination temperatures, the samples were calcined at different temperatures in static air for 3 h. These WO_3/ZrO_2 samples are denoted $WZ\chi(T)$, where T refers to the calcination temperature/°C and χ the tungsten content in weight percent (wt%). For example, WZ10(700) means the sample containing 10 wt% tungsten and calcined at 700 °C. $Pt/WZ\chi(T)$ catalysts were prepared by impregnation using an aqueous solution of H_2PtCl_6 (40% Pt, Acros Organics). The loaded Pt samples were dried at 110 °C for 12 h, and then calcined at 450 °C in static air for 3 h.

Hydrogen and CO chemisorption uptakes of catalyst were measured using a BELCAT-A instrument equipped with a thermal conductivity detector (TCD). The study was conducted in a quartz tubular reactor. Prior to the H_2 or CO chemisorption the samples were pretreated in air at 450 °C for 3 h, reduced at 250 °C in H_2 for 1 h, and switched to argon for 0.5 h to remove the adsorbed H_2 at 250 °C and then cooling down to the desired temperatures. The H_2 pulse chemisorption was measured at 100 °C under atmospheric pressure. The CO pulse chemisorption was measured at 30 °C under atmospheric pressure and the platinum dispersion was calculated by assuming an adsorption of one CO molecule per surface platinum atom.

Temperature-programmed desorption (TPD) of pre-adsorbed NH_3 was carried out on a BELCAT-A instrument and the evolved ammonia concentration was monitored by a Mass Spectrometer and TCD detector. Prior to NH_3 adsorption, about 0.2 g sample was dehydrated under flowing air at 450 °C for 1 h, and reduced by H_2 at 250 °C, then cooled to 100 °C in He. The NH_3 adsorption was carried out at this temperature for 0.5 h, then He was allowed to flow over the sample for 1.0 h at 100 °C. The sample was then heated from 100 °C to 800 °C with a heating rate of 10 °C min^{-1}. The area under the TCD curve was integrated to determine the relative total acidity of the catalysts.

The deoxygenation of glycerol was carried out in a fixed-bed down-flow reactor made of a stainless steel tube (length, 340 mm; internal diameter, 10.0 mm). The catalyst (2.0 mL, 20–40 mesh) was placed between two layers of quartz sands for each test. A thermocouple was situated in the catalytic bed for measurement of the temperature. Prior to reaction, the catalyst was activated in flowing H_2 (50 ml min^{-1}) from ambient to 250 °C at the rate of 0.5 °C min^{-1} and maintaining that temperature for 1 h at atmospheric pressure. After reduction, the system was cooled to the desired reaction temperature. Reaction conditions were changed to investigate the dependence of the conditions. Details of the reaction conditions are described for each result. Hydrogen from a gas cylinder was depressurized to 4.0 MPa and its flow rate was set by a mass flow controller giving a constant flow of 10 ml min^{-1}. Aqueous solutions of glycerol were continuously pumped into the fixed-bed reactor with a high-pressure pump. Hydrogen and glycerol solution flows were mixed at the inlet of the reactor. Gas and liquid were flowed in co-current down-flow mode through the reactor. At the reactor outlet, the liquid and gas flows were cooled and recovered in the gas-liquid separator. The gas flow was depressurized to atmospheric pressure by a back-pressure regulator.

In addition, we also carried out the reaction test of 1,3-PDO and 1,2-PDO in order to discuss the reaction routes of glycerol deoxygenation. The concentration of these reactants in the aqueous solution was 60 mass%.

The liquid products were analyzed using a SP-6800A GC (Shandong Ruihong chromatogram analysis Co., Ltd, China) equipped with a flame ionization detector (FID) and a capillary column (Alltech EC™-1 capillary column, 30 m × 0.53 mm × 1.2 µm). The quantitative analysis was based on internal standard method using *n*-butanol and 1,4-butanediol as double internal standard. The gas-phase products in the tail gas were analyzed with another GC (Shimadzu GC-2014) equipped with a thermal conductivity detector (TCD). Molar yields were given in all cases at total conversion of glycerol. Product selectivity was calculated as the molecular percentage of all products obtained.

3. Results and discussion

The deoxygenation of glycerol in aqueous phase was carried out over $Pt/WO_3/ZrO_2$ catalysts in a fixed-bed reactor under constant pressure and temperature in the following domain, 2.0–5.0 MPa and 110–140 °C, respectively. Under the given reaction conditions, only the deoxygenation products of 1,3-PDO, 1,2-PDO, *n*-propanol (*n*-PrOH), and *i*-propanol (*i*-PrOH) were formed. Degradation products, *e.g.* 1,2-ethanediol, ethanol, methanol, ethane, methane, CO and CO_2 were not detected in the obtained liquid phase or gas phase. This observation indicates that aqueous phase reforming of glycerol is avoided and the catalyst is not able to cleave C–C bond at the reaction temperature used. 1,3-PDO and *n*-PrOH, which were formed from deoxygenation of internal OH of glycerol, were the major products. 1,2-PDO and *i*-PrOH, which were formed from deoxygenation of terminal OH of glycerol, were the minor products. The yield of the products varied with the catalyst composition, catalysts pretreatment, and the reaction parameters.

The performance of the Pt/WZ10(700) catalysts containing between 1.0 and 4.0 wt% platinum for glycerol deoxygenation has been compared at 130 °C under 4.0 MPa hydrogen pressure. The results shown in Table 1 represent the activity and selectivity after 24 h on-stream; at this time there was a pseudo-steady state, and the catalyst activity was relatively stable. As the platinum content increased from 1.0 to 4.0 wt% there was a uniform increase in the glycerol conversion from 14.2% to 84.5%. The yield of 1,3-PDO increased with platinum content and reached a maximum at 3.0 wt% Pt. Further increase of platinum content caused a decrease in the yield of 1,3-PDO. The increase of platinum content from 1.0 to 4.0 wt% led to a uniform increase of the yield of *n*-PrOH from 7.1% to 56.2%, and yield of *i*-PrOH from 1.4% to 5.3%. Along with platinum content from 1.0 to 4.0 wt%, the 1,3-PDO/1,2-PDO ratio increased distinctly from 8.5 to 37.2. These results indicate that the excess platinum content further promotes excessive consecutive deoxygenation of propanediols to *n*-PrOH. Hence, to get a good conversion of glycerol with high selectivity to 1,3-PDO an optimal amount of platinum should be loaded on WZ10(700).

As shown in Table 1, the hydrogen uptakes on Pt/WZ10(700) catalysts increased with platinum content. However, the degree of increase reduced after the platinum reached 3 wt%. This indicated platinum aggregation on the surface of WZ10(700) with too high Pt loading. The average size of the platinum particles on the surface of WZ10(700) support was determined using the measured amounts of chemisorbed CO and is presented in Table 1, where the particle size increased with increasing platinum content. The concentration of protons and hydride ions formed on $Pt/WO_3/ZrO_2$ from hydrogen molecules increased with hydrogen uptakes.[29,30] The protons and hydride ions formed from molecular hydrogen act as active sites for glycerol deoxygenation and glycerol conversion increased with the concentration of protons and hydride ions. However, the excess amount of protons and hydride ions may enhance the consecutive deoxygenation of propanediols to propanols, which suppress the selectivity towards 1,3-PDO and 1,2-PDO.

The effect of tungsten content on the catalytic activity and the product distributions over 2.0Pt/WZ(700) at 130 °C under 4.0 MPa hydrogen pressure is shown in Table 2. Both the activity and the product distributions are dependent on tungsten content. Glycerol conversion starting from 27.0% over 2.0Pt/WZ5(700) to 41.6% with 2.0Pt/WZ10(700). Further increasing tungsten content to 15 wt% leads to a decrease in glycerol conversion to 29.9%. The highest glycerol conversion of 41.6% and 1,3-PDO yield of 18.3% are achieved on 2.0Pt/WZ10(700). Further increasing tungsten content to 15 wt% leads to the decrease of 1,3-PDO yield to 10.7% and glycerol conversion to 29.9%. The maximum value was found at 10 wt% tungsten which is slightly higher than the theoretical monolayer of WZ supports. It was reported that the acidity present on WZ sample increased with loading of tungsten oxide up to monolayer coverage.[32] The surface concentration of acid sites, *i.e.* acidity (NH_3/nm^2) of WZ

Table 1 Effect of Pt content on glycerol deoxygenation over Pt/WZ10(700) catalyst[a]

				Yield (mol%) [c]				
Catalysts	H_2 uptakes (µmol g^{-1}.cat)	Particle size/nm[b]	Conversion (%)	*i*-PrOH	*n*-PrOH	1,2-PDO	1,3-PDO[d]	1,3-PDO/1,2-PDO
1.0Pt/WZ10	30.6	1.8	14.2	1.4	7.1	0.6	5.1 (35.9)	8.5
2.0Pt/WZ10	59.6	—	41.6	3.4	18.4	1.5	18.3 (44.0)	12.2
3.0Pt/WZ10	68.5	2.4	70.2	5.3	31.0	1.8	32.0 (45.6)	17.7
4.0Pt/WZ10	73.7	3.3	84.5	5.3	56.2	0.6	22.3 (26.4)	37.2

[a] Reaction conditions: 130 °C; 4.0 MPa; 2.0 ml of catalyst was used; The aqueous glycerol (60% wt/wt) was fed at the speed of 0.5 ml h^{-1}; Hydrogen flow rate was 10 ml min^{-1}. Data obtained after 24 h on-stream. [b] Data obtained from CO chemisorption. [c] Molar yields are given in all cases at total conversion of glycerol. [d] Selectivity in brackets.

Table 2 Influence of tungsten content on glycerol deoxygenation over 2.0Pt/WZ(700) catalysts [a]

Catalysts	Conversion (%)	Yield (mol%) [b] *i*-PrOH	*n*-PrOH	1,2-PDO	1,3-PDO [c]	1,3-PDO/1,2-PDO
2.0Pt/WZ5(700)	27.0	2.1	10.2	2.5	12.0 (44.4)	4.8
2.0Pt/WZ10(700)	41.6	3.4	18.4	1.5	18.3 (44.0)	12.2
2.0Pt/WZ15(700)	29.9	2.9	14.4	1.9	10.7 (35.8)	5.6

[a] Reaction conditions: see note in Table 1. [b] Molar yields are given in all cases at total conversion of glycerol. [c] Selectivity in brackets.

Table 3 Surface concentration of acid sites of WZ catalysts with different tungsten content and WZ10 calcined at different temperatures

Catalyst	Acidity (NH_3/nm^2) [a]	Catalyst	Acidity (NH_3/nm^2) [a]
WZ10(500)	2.85	WZ10(800)	3.35
WZ10(600)	3.09	WZ5(700)	2.78
WZ10(700)	3.15	WZ15(700)	2.28

[a] Total number of NH_3 molecules desorbed per nm^2 of catalyst surface area from 120 to 750 °C.

samples with different tungsten content, was measured using TPD of NH_3 and is presented in Table 3. TPD of NH_3 shows that the surface concentration of acid sites increases with tungsten content and reaches its maximum for a WZ10 sample calcined at 750 °C. The surface concentration of acid sites decreases when the WO_3 loading exceeds monolayer coverage.

Table 4 shows the effect of calcination temperature of WZ10 support (10 wt% W loading) on the catalytic performance of 2.0 wt% Pt/WZ10 catalyst in deoxygenation of glycerol at 130 °C under 4.0 MPa hydrogen pressure. The collected data show clearly that the increasing WZ10 calcination temperature led to an increasing glycerol conversion starting from 12.7% over a 2.0 wt% Pt/WZ10(500) sample to 47.5% with a 2.0 wt% Pt/WZ10(800). The WZ10 calcinations temperature also has an influence on the product distribution. The yields of 1,3-PDO increases with WZ10 calcination temperature, reaching a plateau at about 18%, when the calcination temperature reached 700 °C. The yields of 1,2-PDO and *i*-PrOH depended weakly on WZ10 calcination temperature. Increasing WZ10 calcination temperature led to an increase in the yield of *n*-PrOH, which formed in consecutive deoxygenation of propanediols, starting from 4.0% over 2.0 wt% Pt/WZ10(500) to 24.9% with 2.0 wt% Pt/WZ10(800). The surface concentration of acid sites, *i.e.* acidity (NH_3/nm^2) of WZ10 with different calcination temperatures, was measured by TPD of ammonia and is presented in Table 3. Increasing the WZ10 calcination temperature led to an increase in the surface concentration of acid sites starting from 2.85 NH_3/nm^2 on a WZ10(500) sample to 3.35 NH_3/nm^2 on a WZ10(800). The heterolytic activation of H_2 into protons and hydride ions formed on $Pt/WO_3/ZrO_2$ involved in the Lewis acid site.[30,31] Hydrogen molecules were dissociatively adsorbed on Pt sites to form hydrogen atoms which undergo spillover onto the surface of WO_3/ZrO_2 support. The spiltover hydrogen atoms diffuse on the WO_3/ZrO_2 surface to reach Lewis acid sites where each hydrogen atom donates an electron to the Lewis acid and becomes a proton (H^+). The proton is stabilized on the O atom (or platinum atom) adjacent to the Lewis acid site and acts as a protonic acid site. A second spiltover hydrogen atom reacts with the electron trapped by the Lewis acid site to form a hydride ion (H^-), which stabilized on the Lewis acid site. Increasing the WZ calcination temperature is favorable as it increases the concentration of proton and hydride ions on $Pt/WO_3/ZrO_2$.

The influence of reaction temperature on the deoxygenation of glycerol in aqueous-phase was investigated over 2.0 wt% Pt/WZ10(700) catalyst, using conditions described in Table 5. Increasing the reaction temperature has a positive effect on the conversion, as shown in Table 5. As the temperature increases from 110 °C to 140 °C, the glycerol conversion increases from 20.9% to 60.5%, with 1,3-PDO selectivity decreasing from 50.9% to 35.7%. The lower reaction temperature is favorable in terms of the selectivity to 1,3-PDO. When the temperature was above 130 °C, the amount of *n*-PrOH, which is the product of consecutive deoxygenation of PDOs, greatly increased. The ratio of 1,3-PDO to 1,2-PDO exhibited little dependence on the reaction temperature. So the optimal reaction temperature to perform aqueous-phase glycerol deoxygenation over 2.0 wt% Pt/WZ10(700) catalyst is 130 °C.

Reactions were carried out at 2.0, 3.0, 4.0 and 5.0 MPa pressure of H_2 at a constant temperature of 130 °C over the 2.0Pt/WZ10(700) catalyst to determine the effect of hydrogen pressure on the reaction. Table 6 provides the summary of the conversions of 60% glycerol solution at 130 °C under different hydrogen pressures. As shown in Table 6, both glycerol conversion and the yield of 1,3-PDO increased when hydrogen pressure increased from 2.0 MPa to 5.0 MPa. The yields of 1,2-PDO and *i*-PrOH were exhibited little dependence on hydrogen pressure. The 1,3-PDO/1,2-PDO ratio increased with hydrogen pressure. The increase of hydrogen pressure provided a positive effect on the glycerol deoxygenation, which might be due to the increase in the concentration of protons and hydride ions formed from hydrogen on $Pt/WO_3/ZrO_2$.

The effect of initial water content on the performance of glycerol deoxygenation was examined over 2.0Pt/WZ10(700) catalyst at 130 °C and 4 MPa pressure of H_2. The results are shown in Table 7. The conversion of glycerol increased with initial water content. It is important that the increase of initial water content from 20% to 80% led to a increase of the selectivity to 1,3-PDO from 39.9% to 49.8%. Interestingly, the selectivity to 1,2-PDO exhibited a reverse trend to that of 1,3-PDO. The 1,3-PDO/1,2-PDO ratio increased distinctly along with initial water content from 20% to 80% and the maximum was as high as 16.5. It was obvious that water is a good solvent for the glycerol deoxygenation over 2.0Pt/WZ10(700). Considering water is a by-product of the glycerol deoxygenation, this property is promising. On the basis of the above observation, we can

Table 4 Influence of WZ10 calcination temperatures on the performance of 2.0Pt/WZ10 catalysts

Catalysts	Conversion (%)	Yield (mol%) [b] *i*-PrOH	*n*-PrOH	1,2-PDO	1,3-PDO [c]	1,3-PDO/1,2-PDO
2.0Pt/WZ10(500)	12.7	1.0	4.0	1.7	6.0 (47.3)	3.5
2.0Pt/WZ10(600)	35.7	3.1	15.3	1.6	15.7 (44.0)	9.8
2.0Pt/WZ10(700)	41.6	3.4	18.4	1.5	18.3 (44.0)	12.2
2.0Pt/WZ10(800)	47.5	3.3	24.9	0.95	18.3 (38.6)	19.3

[a] Reaction conditions: see note in Table 1. [b] Molar yields are given in all cases at total conversion of glycerol. [c] Selectivity in brackets.

Table 5 Influence of reaction temperature on glycerol deoxygenation over the 2.0Pt/WZ10(700) catalyst [a]

Reaction $T/°C$	Conversion (%)	Yield (mol%) [b] *i*-PrOH	*n*-PrOH	1,2-PDO	1,3-PDO [c]	1,3-PDO/1,2-PDO
110	20.9	1.8	7.4	1.0	10.6 (50.9)	10.6
120	33.0	3.0	13.7	1.45	14.9 (45.2)	10.2
130	41.6	3.4	18.4	1.5	18.3 (44.0)	12.2
140	60.5	5.4	31.6	1.9	21.6 (35.7)	11.6

[a] Reaction conditions: see note in Table 1 except the reaction temperature. [b] Molar yields are given in all cases at total conversion of glycerol. [c] Selectivity in brackets.

Table 6 Influence of hydrogen pressure on glycerol deoxygenation over the 2.0Pt/WZ10(700) catalyst [a]

Pressure/MPa	Conversion (%)	Yield (mol%) [b] *i*-PrOH	*n*-PrOH	1,2-PDO	1,3-PDO [c]	1,3-PDO/1,2-PDO
2.0	15.6	2.3	6.4	1.8	5.1 (32.5)	2.8
3.0	33.8	3.3	16.2	1.7	12.6 (37.3)	7.5
4.0	41.6	3.4	18.4	1.5	18.3 (44.0)	12.2
5.0	45.4	3.7	19.1	1.8	20.8 (45.8)	11.5

[a] Reaction conditions: see note in Table 1 except the hydrogen pressure. [b] Molar yields are given in all cases at total conversion of glycerol. [c] Selectivity in brackets.

suggest that water as a protic solvent facilitated the transfer of the formed proton that acts as a Brønsted acid in the liquid reaction. The freely transferable protons can overcome the steric hindrance to the internal OH in glycerol such that the internal OH has almost accessibility for activation as the terminal OH. Nimlos *et al.*[33] reported that the proton affinity for the internal hydroxyl group in glycerol was 195.4 kcal mol^{-1}, while that for the terminal hydroxyl group was 194.8 kcal mol^{-1}, which means that the internal hydroxyl group in glycerol is easier to activate when it has the same exposure to protons. This would explain the higher selectivity for 1,3-PDO when the reaction was performed in dilute aqueous solution.

As a representative example, a time-on-stream behavior of aqueous-phase deoxygenation of glycerol over 2.0Pt/WZ10(700) catalyst was examined for a period of 50 h at 130 °C and 4 MPa, and the results are shown in Fig. 1. The catalyst shows a large increase in glycerol conversion and in the yields of 1,3-PDO and *n*-PrOH with increase in the reaction time up to 8 h. Upon further increasing the reaction time, the yields of 1,3-PDO, 1,2-PDO and *i*-PrOH are stable, even though there is a slight decrease in glycerol conversion and in the yield of *n*-PrOH. This suggests that glycerol is converted to *n*-PrOH by a different pathway. The gradual decrease in glycerol conversion might be due to some loss of activity in the consecutive deoxygenation of propanediols to *n*-PrOH.

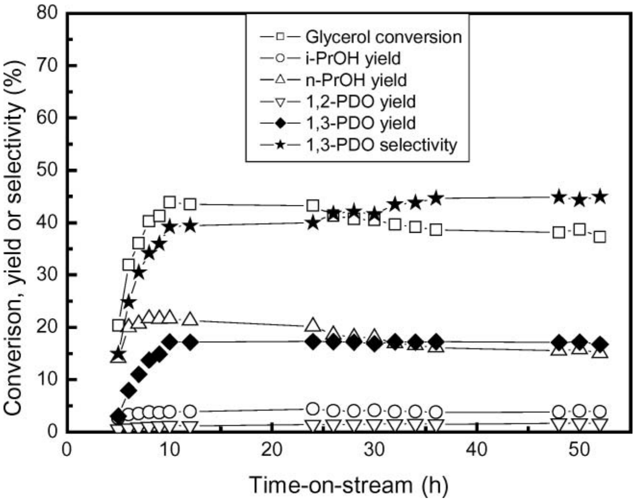


Fig. 1 Time-on-stream behavior of aqueous-phase deoxygenation of glycerol over 2.0Pt/WZ10(700) catalyst. Reaction conditions: 130 °C; 4.0 MPa; 4 mL (5 g) of catalyst was used; The aqueous glycerol (60% wt/wt) was fed at the speed of 1.0 mL h^{-1}; Hydrogen flow rate was 40 mL min^{-1}.

In order to explain the reaction scheme and the product distribution of glycerol deoxygenation, the deoxygenation of

Table 7 Influence of initial water content on the performance of glycerol deoxygenation over the 2.0Pt/WZ10(700) catalyst[a]

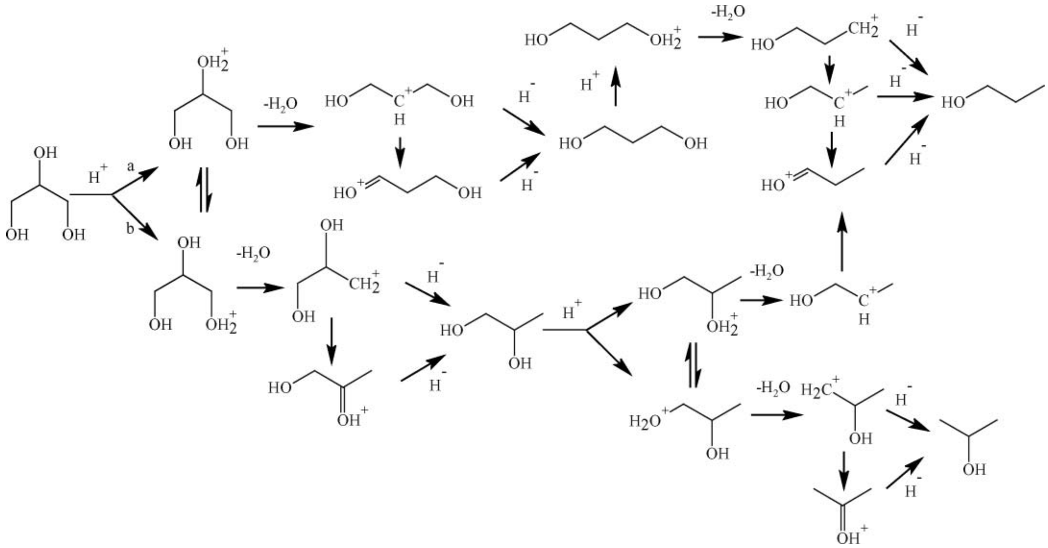
		Yield (mol%) [b]				
Initial water content (wt%)	Conversion (%)	*i*-PrOH	*n*-PrOH	1,2-PDO[c]	1,3-PDO[c]	1,3-PDO/1,2-PDO
80	59.9	4.1	24.1	1.8 (3.1)	29.8 (49.8)	16.5
60	43.6	3.5	17.4	1.5 (3.5)	21.2 (48.6)	14.1
40	41.6	3.4	18.4	1.5 (3.6)	18.3 (44.0)	12.2
20	20.8	2.0	9.4	1.0 (4.8)	8.3 (39.9)	8.3

[a] Reaction conditions are the same as in Table 1 except initial water content. [b] Molar yields are given in all cases at total conversion of glycerol. [c] Selectivity in brackets.

Table 8 Results of deoxygenation of 1,2-PDO, 1,3-PDO and glycerol over 2.0Pt/WZ10(700) catalyst [a]

			Selectivity (mol%)			
Reactant	Reaction *T*/°C	Conversion (%)	*i*-PrOH	*n*-PrOH	1,2-PDO	1,3-PDO
1,2-PDO	120	60.8	9.6	90.3	—	0.0
	130	78.3	9.2	90.7	—	0.0
	140	91.4	10.2	89.7	—	0.0
1,3-PDO	120	12.0	0.0	99.9	0.0	—
	130	22.0	0.0	99.9	0.0	—
	140	36.8	0.0	99.9	0.0	—
Glycerol	120	33.0	9.0	41.4	4.4	45.2
	130	41.6	8.2	44.2	3.6	44.0
	140	60.5	9.0	52.2	3.1	35.7

[a] Reaction conditions: 130 °C; 4.0 MPa; 2.0 ml of catalyst was used; The aqueous reactant (60% wt/wt) was fed at the speed of 0.5 ml h^{-1}; Hydrogen flow rate was 10 mL min^{-1}. TOS = 24 h.



Scheme 1 Proposed reaction mechanism of glycerol deoxygenation over Pt/WZ

1,2-PDO and 1,3-PDO over 2.0Pt/WZ10(700) were also tested under similar conditions as used for glycerol. The results are listed in Table 8. Regarding the conversion of reactants, 1,3-PDO was much lower than 1,2-PDO and glycerol. The reactivity of 1,2-PDO can be much higher than that of 1,3-PDO, and this can explain that the selectivity of 1,3-PDO was much higher than 1,2-PDO in deoxygenation of glycerol. In addition, the formation of *n*-PrOH and *i*-PrOH was observed on Pt/WZ10 in the glycerol reaction. The selectivity to *n*-PrOH was much higher than that to *i*-PrOH in the deoxygenation of 1,2-PDO, the ratio of *n*-PrOH to *i*-PrOH is 7.0, which can explain that the selectivity of *n*-PrOH was much higher than *i*-PrOH in deoxygenation of glycerol. The *n*-PrOH/*i*-PrOH ratio in the glycerol deoxygenaton was similar to that in the 1,2-PDO deoxygenation, and this suggests that *n*-PrOH and *i*-PrOH are mainly formed *via* 1,2-PDO in the glycerol deoxygenation. It shows high regioselectivity for removing the internal hydroxyl group over Pt/WZ10 catalyst. In the deoxygenation of glycerol, the main product was 1,3-PDO and *n*-PrOH, and this means that the formation rate of 1,3-PDO is high and its conversion rate is relatively low, which is supported by the result in Table 8.

The proposed reaction mechanism of glycerol deoxygenation over Pt/WO_3/ZrO_2 is shown in Scheme 1. The mechanisms involved heterolytic cleavage of hydrogen molecules on catalyst to form protons and hydride ions, and then sequentially delivering H^+ followed by H^- to glycerol and diols.

4. Conclusions

This study has demonstrated that the aqueous-phase deoxygenation of glycerol to 1,3-PDO is catalyzed by Pt/WO_3/ZrO_2 catalyst in a fixed-bed continuous flow reactor at relatively lower temperatures (110–140 °C). Aqueous-phase reforming and degradation of glycerol over Pt/WO_3/ZrO_2 catalyst can be avoided at the lower reaction temperature. The predominant products are 1,3-PDO and *n*-propanol. The high selectivity, giving 1,3-PDO and *n*-propanol rather than 1,2-PDO and *i*-propanol, is due to the protonic acid-catalyzed dehydration preferring dehydration at the secondary over the primary OH in the glycerol and diol. Both the conversion of glycerol and the yield of the products significantly varied with the catalyst composition, catalyst pretreatment, and the reaction parameters. A 45.6% selectivity of 1,3-PDO, with 1,3-PDO/1,2-PDO ratio of 17.7 was achieved at 70.2% conversion, 130 °C and 4 MPa over 3.0 wt% Pt/WO_3/ZrO_2 catalyst. The deoxygenation of glycerol is proposed to occur by an ionic mechanism, involving proton transfer and hydride transfer steps.

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References

1 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411–2502.
2 M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. D. Pina, *Angew. Chem., Int. Ed.*, 2007, **46**, 4434–4440.
3 Y. Zheng, X. Chen and Y. Shen, *Chem. Rev.*, 2008, **108**, 5253–5277.
4 A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**, 13–30.
5 C. Zhou, J. N. Beltramini, Y. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527–549.
6 G. W. Huber, J. W. Shabaker and J. A. Dumesic, *Science*, 2003, **300**, 2075–2077.
7 J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel and C. Rosier, *Green Chem.*, 2004, **6**, 359–361.
8 M. A. Dasari, P. P. Kiatsimkul, W. R. Sutterlin and G. J. Suppes, *Appl. Catal., A*, 2005, **281**, 225–231.
9 T. Miyazawa, Y. Kusunoki, K. Kunimori and K. Tomishige, *J. Catal.*, 2006, **240**, 213–321.
10 S. Wang and H. Liu, *Catal. Lett.*, 2007, **117**, 62–67.
11 I. Furikado, T. Miyazawa, S. Koso, A. Shimao, K. Kunimori and K. Tomishige, *Green Chem.*, 2007, **9**, 582–588.
12 T. Kurosaka, H. Maruyama, I. Naribayashi and Y. Sasaki, *Catal. Commun.*, 2008, **9**, 1360–1363.
13 L. Huang, Y. Zhu, H. Zheng, Y. Li and Z. Zeng, *J. Chem. Technol. Biotechnol.*, 2008, **83**, 1670–1675.
14 J. Feng, H. Fu, J. Wang, R. Li, H. Chen and X. Li, *Catal. Commun.*, 2008, **9**, 1458–1464.
15 L. Ma, D. He and Z. Li, *Catal. Commun.*, 2008, **9**, 2489–2495.
16 Z. Huang, F. Cui, H. Kang, J. Chen, X. Zhang and C. Xia, *Chem. Mater.*, 2008, **20**, 5090–5099.
17 A. Alhanash, E. F. Kozhevnikova and I. V. Kozhevnikov, *Catal. Lett.*, 2008, **120**, 307–311.
18 A. Zeng and H. Biebl, *Adv. Biochem. Eng. Biotechnol.*, 2002, **74**, 237–257.
19 K. Wang, M. C. Hawley and S. J. DeAthos, *Ind. Eng. Chem. Res.*, 2003, **42**, 2913–2923.
20 T. M. Che, *U. S. Patent*, 4642394, 1987.
21 M. Schlaf, P. Ghosh, P. J. Fagan, E. Hauptman and R. M. Bullock, *Angew. Chem., Int. Ed.*, 2001, **40**, 3887–3890.
22 M. Schlaf, P. Ghosh, P. J. Fagan, E. Hauptman and R. M. Bullock, *Adv. Synth. Catal.*, 2009, **351**, 789–800.
23 A. Shimao, S. Koso, N. Ueda, Y. Shinmi, I. Furikado and K. Tomishige, *Chem. Lett.*, 2009, **38**, 540–541.
24 Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa and K. Tomishige, *Appl. Catal., B*, 2010, **94**, 318–326.
25 L. Huang, Y. Zhu, H. Zheng, G. Ding and Y. Li, *Catal. Lett.*, 2009, **131**, 312–320.
26 M. Hino and K. Arata, *J. Chem. Soc., Chem. Commun.*, 1988, 1259–1260.
27 X. Chen, C. Chen, N. Xu, S. Han and C. Mou, *Catal. Lett.*, 2003, **85**, 177–182.
28 X. Chen, C. Chen, N. Xu and C. Mou, *Catal. Today*, 2004, **93–95**, 129–134.
29 X. Chen, Y. Du, C. Chen, N. Xu and C. Mou, *Catal. Lett.*, 2006, **111**, 187–193.
30 S. Triwahyono, T. Yamada and H. Hattori, *Appl. Catal., A*, 2003, **242**, 101–109.
31 S. Triwahyono, A. A. Jalil and H. Hattori, *J. Nat. Gas Chem.*, 2007, **16**, 252–257.
32 C. D. Baertsch, S. L. Soled and E. Iglesia, *J. Phys. Chem. B*, 2001, **105**, 1320–1330.
33 M. R. Nimlos, S. J. Blanksby, X. Qian, M. E. Himmel and D. K. Johnson, *J. Phys. Chem. A*, 2006, **110**, 6145–6156.