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Catalytic dehydration of 1,2-propanediol into propanal

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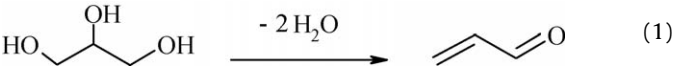
ABSTRACT

Vapor-phase catalytic dehydration of 1,2-propanediol was investigated over several catalysts, such as acidic oxides and supported heteropoly acids. These acids catalyze the dehydration of 1,2-propanediol to produce propanal. In particular, silica-supported silicotungstic acid showed the highest catalytic activity in the formation of propanal. At low conversions, however, propanal reacted with another 1,2-propanediol to produce a cyclic acetal (2-ethyl-4-methyl-1,3-dioxolane). Such acetal formation reduced the selectivity to propanal. Under optimum reaction conditions, 100% conversion was attained with propanal selectivity higher than 93 mol% at 200 °C.

1. Introduction

Catalytic conversion of carbon-neutral biomass into valuable chemicals is expected to reduce damage to the environment [1,2]. Renewable biomass fuels, such as biodiesel, i.e. fatty acid methyl esters, are increasing every year. In the manufacture of biodiesel fuel, glycerol is produced as a by-product for ca. 10% of the manufactured fuel and is one of such promising renewable resources. Glycerol is dehydrated to produce acrolein and hydroxyacetone: acidic catalysts are effective in producing acrolein [3–8], and copper metal selectively catalyzes the dehydration of glycerol into hydroxyacetone [9–11], which can be readily hydrogenated into 1,2-propanediol [12–14].



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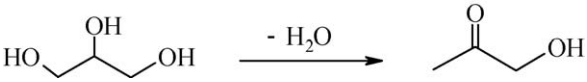

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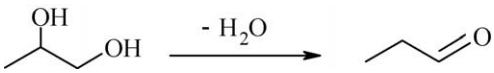
We have previously investigated the conversion of polyols over various types of catalysts. Dehydration of diols, such as 1,3-, 1,4-, and 1,5-diols [15–19], proceeds over rare earth oxides (REOs) to produce unsaturated alcohols. Heavy REO catalysts, such as Tb_4O_7, Er_2O_3, and Yb_2O_3, are selective for the production of 3-buten-1-ol from 1,4-butanediol [17,18]. CeO_2 is the most selective catalyst for the formation of 3-buten-2-ol and *trans*-2-buten-1-ol from 1,3-buanediol [15,16]. Although 1,2-butanediol is dehydrated to produce butanal over CeO_2, its reactivity is low [15].

In the dehydration of 1,3-butanediol, solid acid catalysts have no selectivity: a lot of dehydrated products are formed [20]. Supported heteropoly acids (HPAs) show excellent catalytic activity for the dehydration of glycerol to produce acrolein [6–8]. Since acidic catalysts can preferentially remove a secondary OH group of glycerol first, it is expected that propanal can be formed from 1,2-propanediol over acidic catalysts. Actually, such a strong acid as silica-supported phosphotungstic acid ($H_3PW_{12}O_{40}$) shows some activity for the dehydration of 1,2-proanediol into propanal, together with the formation of the corresponding dioxolanes [21]. Unfortunately, only a few examples have been presented for the production of propanal from 1,2-propanediol.



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This process is expected to be an option of the propanal production because 1,2-propanediol can be derived from glycerol, a renewable resource [12–14]. We have preliminarily found that silicotungstic acid ($H_4SiW_{12}O_{40}$) was active for the formation of propanal from 1,2-propanediol. In this research, we investigated catalytic activity of supported $H_4SiW_{12}O_{40}$ for the reaction of 1,2-propanediol. In this paper, we discuss the catalytic behavior of supported $H_4SiW_{12}O_{40}$ for the reaction of 1,2-propanediol in comparison with the reaction of glycerol.

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Table 1
Catalytic conversion of 1,2-propanediol over several catalysts.[a].

Catalyst	SA ($m^2\ g^{-1}$)	Reaction temp. (°C)	Conversion (%)	Selectivity (mol%)[b]			
				Propanal	Dioxolane	Acetone	2P1ol
SiO_2 (Q-10)	310	400	2.7	41.8	10.3	5.2	9.6
ZrO_2	100	400	93.8	22.8	0.3	12.3	0
TiO_2	50	350	98.2[c]	17.7	0.1	23.3	0
Al_2O_3	195	300	90.1[d]	24.5	28.5	4.0	3.2
SiO_2–Al_2O_3	440	250	68.0	42.6	41.2	1.8	1.9
Amberlyst 15	42	200	94.2	27.4	51.9	0.6	13.3
Q10-SiW-30	220	200	98.4	67.5	22.7	0.9	0.7

[a] Conversion and selectivity were calculated by collecting the effluent produced between the initial 1 and 5 h after each reaction was proceeded $W/F = 0.3/1.7$ g h cm^{-3} where W and F are weight of catalysts and flow rate of 100% 1,2-propanediol of fed reactant, respectively. The flow rate of N_2 as a carrier = 30 $cm^3\ min^{-1}$.
[b] Dioxolane, 2-ethyl-4-methyl-1,3-dioxolane; 2P1ol, 2-propene-1-ol. Other by-products are 1-propanol, propanoic acid, 2-ethyl-2-butenal, and several unknown products; the by-products are not listed in this table.
[c] The selectivity to 1-propanol, 19.3 mol%.
[d] The selectivity to 1-propanol, 27.7 mol%.

2. Experimental

2.1. Samples

1,2-Propanediol was purchased from Wako Pure Chemical Industries, Japan. The alcohol was used for the catalytic reaction without further purification. Three different silicas with mean pore diameters of 3 nm, 6 nm, and 10 nm (CARiACT Q-3, Q-6, and Q-10, respectively) were supplied by Fuji Silycia Chemical Ltd. The pore-size distribution of the silica support was measured by N_2 adsorption at −196 °C; the pore-size distribution is shown in Fig. 1 of Ref. [6]. Al_2O_3 (DC2282), anatase TiO_2 (JRC-TIO-4), and monoclinic ZrO_2 (RSC100) were supplied from Dia Catalyst, Catalyst Society of Japan, and Daiichi Kigenso Kagaku Kogyo Co. Ltd., respectively. SiO_2–Al_2O_3 (N631L) was purchased from Nikki Chemical. An acidic ion-exchange resin, Amberlyst 15, was purchased from Organo Co., Japan. Phosphotungstic acid ($H_3PW_{12}O_{40}{\cdot}nH_2O$, hereafter abbreviated to PW), silicotungstic acid ($H_4SiW_{12}O_{40}{\cdot}24H_2O$, SiW), and phosphomolybdic acid ($H_3PMo_{12}O_{40}{\cdot}nH_2O$, PMo) were purchased from Wako Pure Chemical Industries Ltd., Japan.

Supported catalysts were prepared by an impregnation method, according to the previous report [6]. A prescribed amount of acid component was dissolved in distilled water, and the silica with the particle size ranging from 75 to 500 μm was added to the solution, forming a slurry. The slurry was stirred and the water in the slurry was evaporated under vacuum in a rotary evaporator until it was dried at ambient temperature. Then, the obtained solid was further dried at 110 °C for 2 h. Hereafter, silica-supported HPA catalysts are expressed as Q$a-b-c$ (where a is a mean pore diameter of silica, b is an abbreviated name of the acid component, and c is the amount of catalyst loaded in wt.%). For example, Q10-SiW-30 means 30 wt.% SiW supported on silica CARiACT Q-10. In addition, SiW supported on alumina (DC2282) is written as Al_2O_3-SiW-30. The BET surface areas (and pore volumes) of the silicas are as follows: Q-3, 733 $m^2\ g^{-1}$ (0.455 $cm^3\ g^{-1}$); Q-6, 466 $m^2\ g^{-1}$ (0.822 $cm^3\ g^{-1}$); Q-10, 310 $m^2\ g^{-1}$ (1.13 $cm^3\ g^{-1}$) [6].

2.2. Catalytic reactions

The catalytic reactions were performed in a fixed-bed down-flow reactor. Prior to the reactions, a catalyst sample (weight, $W = 0.30$ g) was preheated in the flow reactor in N_2 flow at the reaction temperature for 1 h. Then, a reactant solution was fed through the top of the reactor at a liquid feed rate, F, of 1.70 $cm^3\ h^{-1}$ together with an N_2 flow of 30 $cm^3\ min^{-1}$. Either pure 1,2-propanediol or an aqueous solution was used as a reactant solution. The effluent collected at 0 °C every hour was analyzed using a gas chromatograph (GC-8A, Shimadzu, Japan) with a flame ionization detector and a 30-m capillary column (TC-WAX, GL Science Inc., Japan) and using a gas chromatograph with a mass spectrometer (GCMS-QP-5050A, Shimadzu, Japan) and a 30-m capillary column (DB-WAX, Agilent Technologies, USA).

In this paper, the catalytic activity was evaluated by averaging the conversion data in the period between 1 and 5 h after the reaction had been initiated. The conversion of alcohol is defined as the amount of 1,2-propanediol consumed in the reaction. The selectivity to each product is expressed as molar selectivity.

2.3. Characterization of catalysts

The specific surface area of the catalysts, SA, was calculated with the BET method using N_2 isotherms at −196 °C.

3. Results

3.1. Reaction of 1,2-propanediol over catalysts

Table 1 lists the catalytic activity values of typical solid acids at various temperatures. The selectivity to propanal over silica, zirconia, titania, alumina, silica–alumina, and amberlyst 15 was low because several by-products, such as 2-ethyl-4-methyl-1,3-dioxolane (hereafter shortened into dioxolane), acetone, 2-propen-1-ol, and other unknown products, were produced. Silica-supported SiW showed high conversion of 1,2-propanediol, and the selectivity to propanal was the highest among all of solid acid catalysts. Dioxolane, the main by-product, was produced in the formation of cyclic acetal from propanal and 1,2-propanediol.

Table 2 summarizes the conversion and the selectivity over HPAs supported on silica with different sizes of mesopore and SiW supported on alumina at 200 °C. For Q10-SiW-30, the conversion and the selectivity to propanal were higher than the values for other HPA catalysts such as Q10-PMo-30 and Q10-PW-30. Compared to the catalytic activity with different amount of SiW in the silica-supported catalysts, high selectivity to propanal was obtained over Q10-SiW-30. Compared to the catalytic activity in the SiW supported on silica with different sizes of mesopore, high conversion and selectivity to propanal were obtained over Q10-SiW-30. The catalytic activity of Q3-SiW-30, Q6-SiW-30, and Al_2O_3-SiW-30 were lower than that of Q10-SiW-30.

3.2. Reaction of 1,2-propanediol over supported heteropoly acid catalysts

Fig. 1 shows changes in the conversion and selectivity over Q10-SiW-30 with time on stream. The selectivity to propanal was

Table 2
Catalytic conversion of 1,2-propanediol over supported HPA catalysts at 200 °C.[a].

Catalyst	SA ($m^2\ g^{-1}$)	Conversion (%)	Selectivity (mol%)[b]				
			Propanal	Dioxolane	Acetone	2P1ol	2M2Pal
Q10-PMo-30	240	9.1	8.2	63.4	0	0.7	0.1
Q10-PW-30	225	90.5	39.2	49.2	1.4	1.4	2.3
Q10-SiW-10	242	84.3	36.5	54.0	4.3	2.2	1.5
Q10-SiW-20	227	97.9	53.1	36.5	2.2	0.9	4.3
Q10-SiW-30	221	98.4	67.5	22.7	0.9	0.7	4.8
Q10-SiW-40	180	96.4	54.3	34.8	2.0	1.1	4.8
Q6-SiW-30	309	90.4	42.1	43.1	1.3	1.2	3.7
Q3-SiW-30	327	22.1	3.2	80.6	1.1	1.4	0.8
Al_2O_3-SiW-30	181	14.8	0.5	83.8	0.1	2.3	0.0

[a] Conversion and selectivity were averaged in the initial 1–5 h. $W/F = 0.3/1.7$ g h cm^{-3} where W and F are catalyst weight and flow rate of 100% 1,2-propanediol fed, respectively. N_2 carrier flow rate = 30 $cm^3\ min^{-1}$.
[b] Dioxolane, 2-ethyl-4-methyl-1,3-dioxolane; 2P1ol, 2-penten-1-ol; 2M2Pal, 2-methyl-2-pentenal. Other by-products are propanoic acid and several unknown products.

decreased with increasing time on stream, and that to dioxolane was increased with increasing time on stream.

We conducted the further research under various reaction conditions for inhibiting the degradation of Q10-SiW-30, as shown in Tables 3–6. Table 3 shows the results of dehydration of 1,2-propanediol over Q10-SiW-30 with several values of the concentration of aqueous 1,2-propanediol solution. The conversion level of 1,2-propanediol was almost the same with different concentrations. However, the selectivity to propanal increased with decreasing concentration of 1,2-propanediol.

Table 4 shows the dependence of the conversion over Q10-SiW-30 on temperature. The conversion and selectivity to propanal increased with increasing reaction temperature. The catalytic activity at 240 °C, however, was lower than that at 220 °C. Table 5 shows dependence of the conversion over Q10-SiW-30 on the weight of catalyst used. Complete conversion of 1,2-propanediol was attained above 0.3 g, with propanal selectivity higher than 93 mol%.

Table 6 lists the dependence of carrier gas on the catalytic activity. When a mixture of NH_3 and N_2 gases was flowed prior to the reaction, the catalytic activity was much lower than that without pretreatment. Acidic carbon dioxide as a carrier gas did not affect the catalytic reaction. The catalytic activity in N_2 carrier gas was the highest among gases.

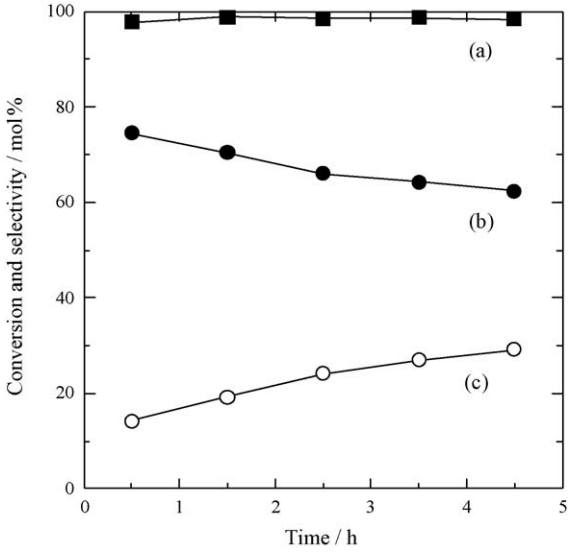

Fig. 1. Changes in the conversion and selectivity in the dehydration of 1,2-propanediol over Q10-SiW-30 with time on stream. (a) Conversion of 1,2-propanediol, (b) selectivity to propanal, (c) selectivity to 2-ethyl-4-methyl-1,3-dioxolane over Q10-SiW-30 with catalyst weight of 0.30 g at 200 °C in feed rate of 100 wt.% 1,2-propanediol of 1.7 $cm^3\ h^{-1}$ and N_2 carrier flow of 30 $cm^3\ min^{-1}$. The averaged data are listed in Table 3.

4. Discussion

4.1. Difference in the catalytic activities of HPAs

Silica-supported SiW showed the highest catalytic activity among all of silica-supported HPAs used in this work, including SiW, PW and PMo (Table 2). On the other hand, the catalytic activity of supported PMo showed the lowest catalytic activity. It is reported that the order of acid strength of crystalline HPAs is PW > SiW > PMo, but the stability to hydrolysis in solution is reported in the order of SiW, PW, and PMo [22]. For some reactions, SiW shows the highest catalytic activity among HPAs; most of those reactions relate to water [23]. This reaction is dehydration of 1,2-propanediol, and the presence of water producing in the reaction atmosphere is considered to be the reason why SiW showed the highest catalytic activity, as is shown in Table 3.

Table 3
Effects of concentration of 1,2-propanediol in the presence or absence of water over Q10-SiW-30 catalyst at 200 °C.[a].

Concentration of reactant (wt.%)	Conversion (%)	Selectivity (mol%)[b]				
		Propanal	Dioxolane	Acetone	2P1ol	2M2Pal
100	98.4	67.5	22.7	0.9	0.7	4.8
80	97.8	72.9	16.9	1.6	2.0	4.6
50	96.9	81.2	7.5	2.8	3.8	3.0
30	99.6	92.2	1.6	2.4	0.4	3.2

[a] Conversion and selectivity were averaged in the initial 1–5 h. $W/F = 0.3/1.7$ g h cm^{-3} where W and F are catalyst weight and flow rate of 1,2-propanediol solution fed, respectively. N_2 carrier flow rate = 30 $cm^3\ min^{-1}$.
[b] Abbreviations of products' name are the same as those in Table 2.

Table 4
Effects of reaction temperature in the conversion of 1,2-propanediol in the presence of water over Q10-SiW-30 catalyst.[a].

Temperature (°C)	Conversion (%)	Selectivity (mol%)[b]				
		Propanal	Dioxolane	Acetone	2P1ol	2M2Pal
160	73.3	53.1	35.7	2.1	3.3	2.5
180	94.7	85.7	7.7	1.9	1.1	2.7
200	99.6	92.2	1.6	2.4	0.4	3.2
220	99.7	93.5	1.2	2.1	0	2.5
240	95.2	90.1	3.8	3.5	0.5	1.8

[a] Conversion and selectivity were averaged in the initial 1–5 h. $W/F = 0.3/1.7$ g h cm^{-3} where W and F are catalyst weight and flow rate of 30 wt.% aqueous 1,2-propanediol solution fed, respectively. N_2 carrier flow rate = 30 $cm^3\ min^{-1}$.
[b] Abbreviations of products' name are the same as those in Table 2.

Table 5
Conversion of 1,2-propanediol over Q10-SiW-30 catalysts at different contact time.[a].

Catalyst weight (g)	Contact time (h g-cat g-glycerol^{-1})	Conversion (%)	Selectivity (mol%)[b]				
			Propanal	Dioxolane	Acetone	2P1ol	2M2Pal
0.2	0.39	94.3	81.8	9.2	1.6	1.8	2.7
0.3	0.59	99.6	92.2	1.6	2.4	0.4	3.2
0.6	1.18	100	93.4	0.5	2.0	0.2	2.9
0.9	1.77	100	93.5	0.5	2.2	0.1	2.7

[a] Conversion and selectivity were averaged in the initial 1–5 h at 200 °C. Flow rate of 30 wt.% aqueous glycerol solution fed was 1.7 cm^3 h^{-1}. N_2 carrier flow rate = 30 cm^3 min^{-1}. Contact time is defined as W/F_1 where W and F_1 are catalyst weight and weight flow rate of 1,2-propanediol fed, respectively.
[b] Abbreviations of products' name are the same as those in Table 2.

It is also reported that HPAs such as PW and SiW can be highly dispersed inside mesoporous silica, MCM-41, by supporting up to 40 wt.% of those HPA, but supporting HPAs more than 50 wt.% on silica tends to cause poor dispersion of HPAs because of the formation of small crystals inside the pores of MCM-41 [24]. In this work, silica-supported SiW was prepared with various loading amounts. This work also showed a tendency similar to that of MCM-41 [24], and the optimum amount of loading was 30 wt.% as shown in Table 2. This result indicates that the surface area of Q10-SiW-40 is diminished by increasing the amount of SiW compared to Q10-SiW-30. A large amount of SiW partially closed some of mesopore of silica, and this shrank the size of the reaction field used for reacting 1,2-propanediol. The low activity leads to low selectivity to propanal, because propanal is reacted with 1,2-propandiol to produce dioxolane at low conversion.

Comparison of the silicas with three types of pore sizes clarified the further details (Table 2). The silica with 10 nm in pore diameter was the most effective among three sizes of pores. On the other hand, the catalytic activity of silica with either 3 nm or 6 nm was lower than that with 10 nm, because SiW was dispersed not only on the surface of mesopores but also outside the mesopores. In particular, the mesopores smaller than 6 nm are considered to be partially closed due to the excessive amounts of SiW on silica with the small pore volumes.

Our group has reported that large crystals of SiW are formed in small mesopores of 3 nm due to the aggregation, and such large crystals inside this size of mesopore are less active [6]. Therefore, the large mesopore is necessary for higher efficiency of reaction. This explanation also indicates why the larger size of mesopore is necessary. In addition, the white color of the catalyst was changed into black after the reaction. This is considered to be due to the coking of the catalyst, and carboneous components created by coking on the catalyst also may cause closure of mesopores.

4.2. Reactivity of 1,2-propanediol comparing with glycerol

ZrO_2-supported and TiO_2-supported HPAs show high conversion of 1,2-propanediol, but the selectivity to propanal is low: by-products such as 2-propen-1-ol and acetone are also produced, as shown in Table 1. Amberlyst and SiO_2–Al_2O_3 produce large proportions of dioxolane, which is produced from propanal and 1,2-propanediol by cyclic acetal reactions. This reaction proceeds when excessive 1,2-propanediol is reacted with aldehyde at low conversion. We have studied the acetal formation from carbonyl compound and diol using HPA catalysts, and we have reported that HPAs are effective catalysts to give high yields of cyclic acetal [23]. Others reported that HPAs produce dioxolane as by-product in the hydration of 1,2-propanediol [21]. Judging from the present results, we conclude that dioxolane is produced on the catalyst with relatively strong acidity.

Table 6
Conversion of 1,2-propanediol over Q10-SiW-30 catalysts in different atmospheres.[a].

Carrier gas	Conversion (%)	Selectivity (mol%)[b]				
		Propanal	Dioxolane	Acetone	2P1ol	2M2Pal
N_2	99.6	92.2	1.6	2.4	0.4	3.2
CO_2	97.6	90.0	4.1	1.8	0.7	2.3
N_2 (pretreated in NH_3)[c]	4.0	19.1	60.1	6.8	2.1	0

[a] Conversion and selectivity were averaged in the initial 1–5 h at 200 °C. W/F = 0.3/1.7 g h cm^{-3} where W and F are catalyst weight and flow rate of 30 wt.% aqueous 1,2-propanediol solution fed, respectively. Carrier flow rate = 30 cm^3 min^{-1}.
[b] Abbreviations of products' name are the same as those in Table 2.
[c] An equimolar mixture of N_2 and NH_3 at a flow rate of 30 cm^3 min^{-1} was fed into the reactor for 1 h prior to the reaction.

In the vapor-phase reaction of polyols, glycerol is an analogous reactant to 1,2-propanediol. Here, we discuss the reactivity of the reactants. When the primary OH group of glycerol is eliminated, hydroxyacetone is produced, as shown in reaction scheme (2): this process readily proceeds over copper metal catalysts [11]. In other words, copper catalysts do not show dehydration activity for 1,2-propanediol, but show dehydrogenation activity to produce hydroxyacetone [25]. In the dehydration of glycerol over supported HPAs, acrolein is the major product, as shown in reaction scheme (1) [6]. To produce acrolein, the secondary OH group of glycerol should be eliminated first to produce 3-hydroxypropanal, then the residual OH group could be removed [6]. Protonic acids such as HPAs readily catalyze the dehydration of secondary OH group in alcohol in a way that is controlled by Markownikoff's rule. Acetone, which is produced by eliminating the primary OH group of 1,2-propanediol, is a minor product.

4.3. Reaction scheme of the dehydration of 1,2-propanediol

Fig. 2 shows the reaction route including the side reaction in the hydration of 1,2-propanediol into propanal. Propanal, 2-propen-1-ol, acetone, dioxolane and 2-metyl-2-pentenal are observed in the reaction of 1,2-propanediol. Propanal and acetone would be formed via tautomerization of 1-propen-1-ol and 1-propen-2-ol, respectively. 2-Propen-1-ol competes with the formation of 1-

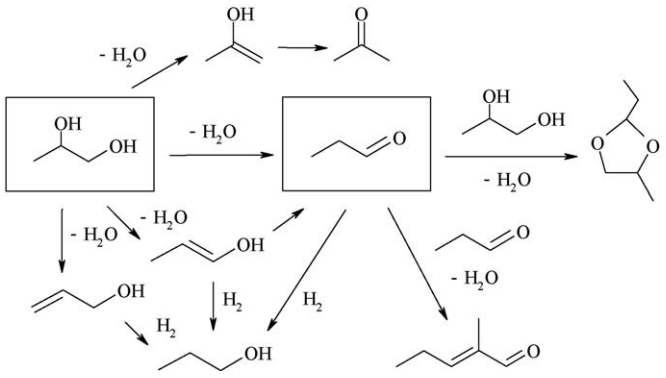

Fig. 2. Reaction route of 1,2-propanediol.

propen-1-ol that is readily converted into propanal. In a density functional theory (DFT) calculation, a protonated form of propanal is more suitable than a protonated form of acetone [26]. It is reasonable that propanal is the major product in the 1,2-propanediol reaction catalyzed by acids. Another DFT study proposed a reaction mechanism for the rearrangement of ethylene glycol to acetaldehyde: a rearrangement with a hydride shift occurring in concert with the loss of water from a protonated glycol shows the lower energy pathway [27].

Dioxolane is produced as a by-product via cyclic acetal formation so as to consume propanal reacted with another 1,2-propanediol, and 2-metyl-2-pentenal was also produced by self-aldol condensation of propanal. In the reactions, dioxaolane should be reduced to achieve high propanal selectivity. In the decomposition of dioxolane, two propanal molecules should be produced. To develop an efficient catalytic process, we have to study and control the decomposition of dioxolane.

5. Conclusions

Acidic inorganic oxides and supported heteropoly acids catalyzed the dehydration of 1,2-propanediol into propanal by vapor-phase catalytic dehydration. Especially, silica-supported silicotungstic acid showed the highest catalytic activity among three silica-supported heteropoly acids: silicotungstic acid, phosphotungstic acid, and phosphomolybdic acid. The main by-product was 2-ethyl-4-methyl-1,3-dioxolane, which was formed by reacting propanal with another diol. It was found that the dioxolane formation was reduced by adding water into the 1,2-propanediol feed solution, and that silica supports with mesopores larger than 6 nm were effective in increasing the catalytic activity. Silicotungstic acid supported on silica with mesopore diameter of 10 nm and loading amount of 30 wt.% is the most active catalyst, and 100% conversion was achieved with propanal selectivity higher than 93 mol% in the reaction of 30 wt.% aqueous 1,2-propanediol solution at 220 °C.

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