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Comparison of gas-phase dehydration of propane polyols over solid acid–base catalysts

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ABSTRACT

Gas-phase dehydration of aqueous propane polyols including glycerol, 1,2- and 1,3-propanediols was investigated over various solid catalysts with a wide range of acid–base properties. Fairly high selectivity (40–75 mol%) for propanal formation from 1,2-propanediol, and acrolein from glycerol was obtained over the catalysts with high fractional acidity in the range of $-8.2 < H_0 \leq -3.0$, in which Brønsted acidity appeared advantageous over Lewis acidity. The dehydration of 1,3-propanediol produced quite scattered products and a clear relationship between its product selectivity and the catalyst acidity could not be established. Mechanistic implications of these observations are discussed, which point to that the dehydration reactions of both 1,2-propanediol and glycerol are initiated by activation of the hydroxyl group bonded with the central carbon atoms.

1. Introduction

Catalytic conversion of renewable biomass-derivate feedstocks to value-added fuels and chemicals has been attracting much attention since traditional fossil resources (oil, coal, natural gas, etc.) could become very limited in a few decades [1–3]. Propane polyols including trihydroxyl propane (or glycerol, GL), 1,2- and 1,3-propanediols (abbreviated as 1,2- and 1,3-PD) are obtainable from secondary conversion of many biomass derivates [4]. Also, the worldwide commercial production of bio-diesel in recent years has increased substantially the availability of GL [5,6]. The surplus production of these propane polyols would made them remarkable and attractive platform molecules for sustainable production of various value-added chemical [7–10]. One of the potential reactions for the utilization of these propane polyols would be the dehydration in the presence of an acid–base catalyst. For instance, selective dehydration of GL to produce acrolein in either liquid or gas phase has been investigated frequently as an important routes for GL utilization and upgrading since acrolein is the intermediate for many important chemicals and materials [11–22,24–30]. However, investigation on the dehydration reactions of 1,3-PD [31,32] and 1,2-PD [33] could be seldom found in literature. Fundamentally, knowledge on the catalytic chemistry for these dehydration reactions of PDs could also help to future our understanding on the reaction mechanism of GL hydrogenolysis over supported transition metal catalysts since the acid–base property of the oxide supports were sometimes found to have significant consequence on the performance of the active metals [8,34].

Our earlier investigation using various unsupported and supported solid acid catalysts for the gas-phase dehydration of aqueous GL has identified that the most efficient acidic sites for acrolein production would be those having the highest acid strength in the range of $-8.2 < H_0 \leq -3.0$ (H_0 being the Hammett acidity function) and Brønsted acid sites are more effective than Lewis acid ones [20]. Most of these earlier catalysts are used here in this study to catalyze the gas-phase dehydration of aqueous 1,2- and 1,3-PD, with a motivation to understand the dependence on the catalyst acidity of their reactivity and product selectivity. In order to show the similarity/dissimilarity between the reactivity and product selectivity of these three polyols over the acid–base catalysts, the dehydration of aqueous 1,2- and 1,3-PD are carried out, to the possible highest extent, under conditions closest to those employed in our earlier study on the catalytic dehydration of aqueous GL [24].

2. Experimental

2.1. Catalyst preparation

CeO_2 and MgO were prepared by air calcination at 500 °C for 4 h of commercial $Ce(NO_3)_3{\cdot}6H_2O$ (AR) and MgO (AR), purchased from

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Sinopharm Chemical Reagent Beijing Co., Ltd. ZrO_2 was prepared by air calcination of a homemade zirconyl hydroxide (hydrogel) at 500 °C for 4 h, the preparation procedure was detailed previously [35,36].

Niobium oxide (Nb_2O_5) catalysts were prepared by air calcining a hydrated niobium oxide ($Nb_2O_5 \cdot nH_2O$, CBMM HY-340) at various temperatures (350–700 °C) for 4 h. According to the calcination temperature, these samples were denoted as Nb_2O_5-T (T = 350, 400, 500 and 700), as in Ref. [21].

Amorphous Al_2O_3 and SiO_2–Al_2O_3 samples were supplied by Fushun Research Institute of Petroleum Processing (FRIPP), SINOPEC, and were calcined at 500 °C in flowing air for 4 h before use.

Microporous molecular sieve materials including SAPO-34 ($SiO_2/Al_2O_3/P_2O_5 = 1/4/3.5$), Hβ ($SiO_2/Al_2O_3 = 26$) and HZSM-5 ($SiO_2/Al_2O_3 = 38$) were supplied by Dr. Zhong-Ming Liu at Dalian Institute of Chemical Physics, Chinese Academy of Sciences, and these materials were also calcined at 500 °C in flowing air for 4 h before use. 15 wt% WO_3/ZrO_2, 5 wt% H_3PO_4/α-Al_2O_3 and 5 wt% SO_4^{2-}/ZrO_2, whose preparation were described in detail in our previous work [20].

All the catalysts were pressed, crushed, and sieved to 20–40 mesh before they were used for the dehydration reactions.

2.2. Catalytic reaction

The gas-phase dehydration reaction of the propanediols (1,2- and 1,3-PD) was carried out at 315 °C under atmospheric pressure in a vertical fixed-bed quartz reactor (i.d. 9 mm, length 50 cm) heated by a tubular furnace (height 40 cm) [20–22,28,30]. A fixed volume of the catalyst (0.63 mL) was sandwiched in the middle section of the reactor, with quartz wool packed at both ends. 2 mL quartz sands were placed above the catalyst bed in order to preheat and ensure complete vaporization of the feed solution. The loaded catalyst was pretreated at 315 °C for 1.5 h in flowing dry nitrogen (30 mL min^{-1}) before the reaction. As in our previous studies of glycerol dehydration reaction [20–22,28,30], an aqueous solution containing 10 mol% 1,2- or 1,3-PD was used as the reaction feed, which was fed into the reactor by a calibrated micro-pump. The catalyst performance including stability and product selectivity of the solid catalysts was evaluated for 10 h with a gas hourly space velocity (GHSV) of 400 h^{-1} by 1,2- or 1,3-PD. The reaction products were condensed in an ice-water trap and collected hourly for analysis on a HP6890 GC equipped with a HiCap CBP20-S25-050 (Shimadzu) capillary column (i.d. 0.32 mm × 25 m) and a FID detector [20–22]. Conversion of the reactant PD and product selectivity were calculated according to the following equations:

$$\text{Propanediol conversion}\quad(\%) = \frac{\text{Moles of propylene glycol reacted}}{\text{Moles of propylene glycol in the feed}} \times 100$$

$$\text{Product selectivity}\quad(\text{mol\%}) = \frac{\text{Moles of carbon in a product defined}}{\text{Moles of carbon in propylene glycol reacted}} \times 100$$

3. Results and discussion

The catalysts investigated in this work are categorized into four groups according to their highest acid or base strength by Hammett function (H_0 or H_-), as measured in our previous work [20]. They are base catalysts of $H_- \geq +7.2$ (Group-1), weak and medium strong acid catalysts of $-3.0 < H_0 \leq +6.8$ (Group-2), strong acid catalysts of $-8.2 < H_0 \leq -3.0$ (Group-3), and very strong acid catalysts of $H_0 \leq -8.2$ (Group-4). Tables 1 and 2 give the measured basicity (Group-1) and acidity data of the catalysts (Groups 2–4) in different base or acid strengths.

Table 1
Basic catalysts and their basicity in different base strengths [20].

Catalyst[a]	BET surface area ($m^2\,g^{-1}$)	Basicity ($mmol\,g^{-1}$)		
		$+7.2 \leq H_- < +15.0$	$+15.0 \leq H_-$	Total
Group-1				
CeO_2	73	0.10	0	0.10
MgO	37	0.04	0.34	0.38

[a] Calcination temperature: 500 °C.

The gas-phase dehydration reactions of 1,2- and 1,3-PD were carried out by passing an aqueous solution containing 10 mol% 1,2- or 1,3-PD at 315 °C at a fixed GHSV of 400 h^{-1} by 1,2- or 1,3-PD. It was generally observed during the reaction that the conversion of 1,2-PD or 1,3-PD declined more or less with the reaction time-on-stream (TOS) and the product selectivity could not be stabilized unless at TOS longer than 2–6 h, as were observed during the dehydration of GL [20–22,28,30]. Tables 3 and 4 show, respectively, the catalyst performance for the dehydration of 1,2- and 1,3-PD during periods of TOS = 1–2 h and 9–10 h; the selectivity for propanal and allyl alcohol are tabulated, respectively, to demonstrate the product selectivity change. The reaction data presented below are those obtained at TOS = 9–10 h, which give more representative (nearly stable) reactant conversion and product selectivity data of the catalytic dehydration reactions.

3.1. Catalytic dehydration of 1,2-PD

Table 5 shows the reactant conversion and product distribution data from the catalytic dehydration of 1,2-PD at TOS = 9–10 h. The conversion of 1,2-PD over the acidic catalysts (Group-2, -3 and -4) was generally higher than 55%, except for Nb_2O_5-700 (20%), 15 wt% WO_3/ZrO_2 (45%) and 5 wt% H_3PO_4/α-Al_2O_3 (30%). The major product was propanal, with a selectivity usually higher than 60 mol%, except for ZrO_2 (5 mol%), Al_2O_3 (40 mol%), 5 wt% H_3PO_4/α-Al_2O_3 (33 mol%) and 5 wt% SO_4^{2-}/ZrO_2 (25 mol%). The other products identified clearly at selectivity of 0.7 mol% or higher were acetone, acetaldehyde, 1-propanol and allyl alcohol; the selectivity for any-one of these by-products was generally no higher than 15 mol%.

The main feature in the product selectivity agrees qualitatively with those reported earlier by Sato et al. [33]. However, the formation of dioxolane and methylpentenal, which were detected in Sato et al's work over SiO_2, Al_2O_3, SiO_2–Al_2O_3 and 30 wt% $H_4SiW_{12}O_{40}/SiO_2$ catalysts at temperatures lower than 200 °C using pure or aqueous 1,2-PD as the reaction feed [33], were uncertain in our study. If these two molecules were produced, their selectivity would be far less than 1 mol% over any catalyst employed in this study. This difference could arise from the much higher reaction temperature (315 °C) and lower 1,2-PD concentration in the feed (10 mol% or 31.9 wt% 1,2-PD in water) employed in this present work. Indeed, Sato et al. also observed that the production of dioxolane was reduced remarkably (from 22.7 mol% to 1.6 mol%) when the concentration of 1,2-PD in the feed was lowered from 100 wt% to 30 wt% [33].

A number of heavier products including carbonaceous residues on the solid catalysts remained unidentified and they were given as the unknowns in the second to the last column of Table 5 [20–22,33]. However, we confirmed with rigorously calibrated GC–MS analysis of the product mixtures that any inter-molecular dehydration reaction of 1,2-PD would be insignificant over all of the catalysts investigated in this study.

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Table 2
Acid catalysts and their acidity in different acid strengths [20].

Catalyst	BET surface area ($m^2\ g^{-1}$)	Acidity ($mmol\ g^{-1}$)			
		$H_0 \leq -8.2$	$-8.2 < H_0 \leq -3.0$	$-3.0 < H_0 \leq +6.8$	Total
Group-2					
ZrO_2[a]	60	0	0	0.10	0.10
Nb_2O_5-700	15	0	0	0.02	0.02
Group-3					
Al_2O_3[a]	331	0	0.42	0.48	0.90
HZSM-5[a]	365	0	0.28	0.36	0.64
Nb_2O_5-400	98	0	0.20	0.14	0.34
15wt%WO_3/ZrO_2[b]	90	0	0.14	0.32	0.46
Nb_2O_5-500	51	0	0.06	0.10	0.16
5wt%$H_3PO_4/\alpha\text{-}Al_2O_3$[c]	4	0	0.01	0.02	0.03
SAPO-34[a]	551	0	0.01	0.05	0.06
Group-4					
5wt%SO_4^{2-}/ZrO_2[d]	118	0.42	0.08	0.18	0.68
SiO_2–Al_2O_3[a]	340	0.12	0.44	0.20	0.76
Hβ[a]	556	0.06	0.70	0.30	1.06
Nb_2O_5-350	109	0.04	0.28	0.20	0.52

[a] Calcination temperature: 500 °C.
[b] Calcination temperature: 900 °C.
[c] Pretreated at 315 °C for 4 h in flowing dry nitrogen.
[d] Calcination temperature: 600 °C.

Compared with the solid acid catalysts, the two basic catalysts CeO_2 and MgO (Group-1) effected much lower 1,2-PD conversion (<25%), as well as much lower selectivity for the formation of propanal (<27 mol%). Acetone appeared instead as a remarkable product over these basic catalysts. We also detected in the product significant selectivity for methanol (5 mol%) and ethanol (8 mol%) when CeO_2 was the catalyst, which is at variance of ref 33 where formation of these two products was not reported. Thus, the solid base catalysts appeared nonselective for the dehydration of 1,2-PD, as in the case of GL dehydration [20]. This would not be surprising as solid base catalysts are known as effective dehydrogenation catalysts in the reaction of mono-alcohols [37].

The last column of Table 5 gives the amount of “carbonaceous” deposits on each used catalyst that had served the reaction up to the point of TOS = 10 h. The carbon deposits were quantitatively measured by temperature-programmed oxidation (TPO) in the TG-DTG mode [21–23]. On correlating the amounts of carbon deposits with the specific surface area and acidity data of the catalysts (Table 2), it is disclosed that the amount of carbonaceous deposits increased essentially with the surface area and acid strength of the catalyst. Secondary reactions induced by the catalytic acid sites could be responsible for the deposition of carbonaceous species at the catalyst surface [37]; the discussion of which is outside the scope of this study.

In order to find out if there is any similarity between the catalytic dehydrations of 1,2-PD and GL over the same series of catalysts, we attempt to correlate in Fig. 1 the (stable) selectivity for propanal in the catalytic dehydration of 1,2-PD (at TOS = 10 h) with the catalyst acid–base strength, as we did for the dehydration of GL for acrolein production [20]. Obviously, the strongly acidic catalysts in Group-3 ($-8.2 < H_0 \leq -3.0$) showed the highest selectivity for propanal as compared to those basic (Group-1: $H_- \geq +7.2$) and acidic catalysts with either weaker (Group-2: $-3.0 < H_0 \leq +6.8$) or stronger acidity (Group-4: $H_0 \leq -8.2$). The selectivity for propanal formation from

Table 3
Catalytic performance of the tested solid acid–base catalysts for the gas-phase dehydration of 1,2-PD at 315 °C.

Catalyst (0.63 mL)	Catalyst amount (g)	TOS = 1–2 h		TOS = 9–10 h	
		X^a (%)	S^b (mol%)	X^a (%)	S^b (mol%)
Group-1 ($+7.2 \leq H_-$)					
CeO_2	0.90	29	10	22	11
MgO	0.36	14	26	10	27
Group-2 ($-3.0 < H_0 \leq +6.8$)					
ZrO_2	0.81	82	3	65	5
Nb_2O_5-700	0.84	25	55	20	57
Group-3 ($-8.2 < H_0 \leq -3.0$)					
Al_2O_3	0.23	97	35	92	33
HZSM-5	0.38	91	74	55	76
Nb_2O_5-400	0.57	95	69	69	72
15 wt%WO_3/ZrO_2	0.71	87	61	45	73
Nb_2O_5-500	0.61	95	55	85	63
5 wt% $H_3PO_4/\alpha\text{-}Al_2O_3$	0.63	44	31	30	40
SAPO-34	0.40	90	63	83	67
Group-4 ($H_0 \leq -8.2$)					
5wt%SO_4^{2-}/ZrO_2	0.71	83	23	60	25
SiO_2–Al_2O_3	0.20	94	53	69	60
Nb_2O_5-350	0.57	98	50	65	65

[a] Conversion of 1,2-PD.
[b] Selectivity for propanal.

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Table 4
Catalytic performance of the tested solid acid–base catalysts for the gas-phase dehydration of 1,3-PD at 315 °C.

Catalyst (0.63 mL)	Catalyst amount (g)	TOS = 1–2 h		TOS = 9–10 h	
		X^a (%)	S^b (mol%)	X^a (%)	S^b (mol%)
Group-1 (+7.2 ≤ H_-)					
CeO_2	0.90	81	88	50	91
MgO	0.36	33	6	13	8
Group-2 (−3.0 < H_0 ≤ +6.8)					
ZrO_2	0.81	30	29	17	33
Nb_2O_5-700	0.84	8	7	5	7
Group-3 (−8.2 < H_0 ≤ −3.0)					
Al_2O_3	0.23	63	14	42	16
HZSM-5	0.38	27	10	11	11
Nb_2O_5-400	0.57	–	–	–	–
15 wt% WO_3/ZrO_2	0.71	82	6	20	11
Nb_2O_5-500	0.61	–	–	–	–
5 wt% H_3PO_4/α-Al_2O_3	0.63	8	10	4	11
SAPO-34	0.40	11	10	8	10
Group-4 (H_0 ≤ −8.2)					
5 wt%SO_4^{2-}/ZrO_2	0.71	–	–	–	–
SiO_2–Al_2O_3	0.20	73	11	47	13
Hβ	0.23	29	15	12	16
Nb_2O_5-350	0.57	67	19	48	20

[a] Conversion of 1,3-PD.
[b] Selectivity for allyl alcohol.

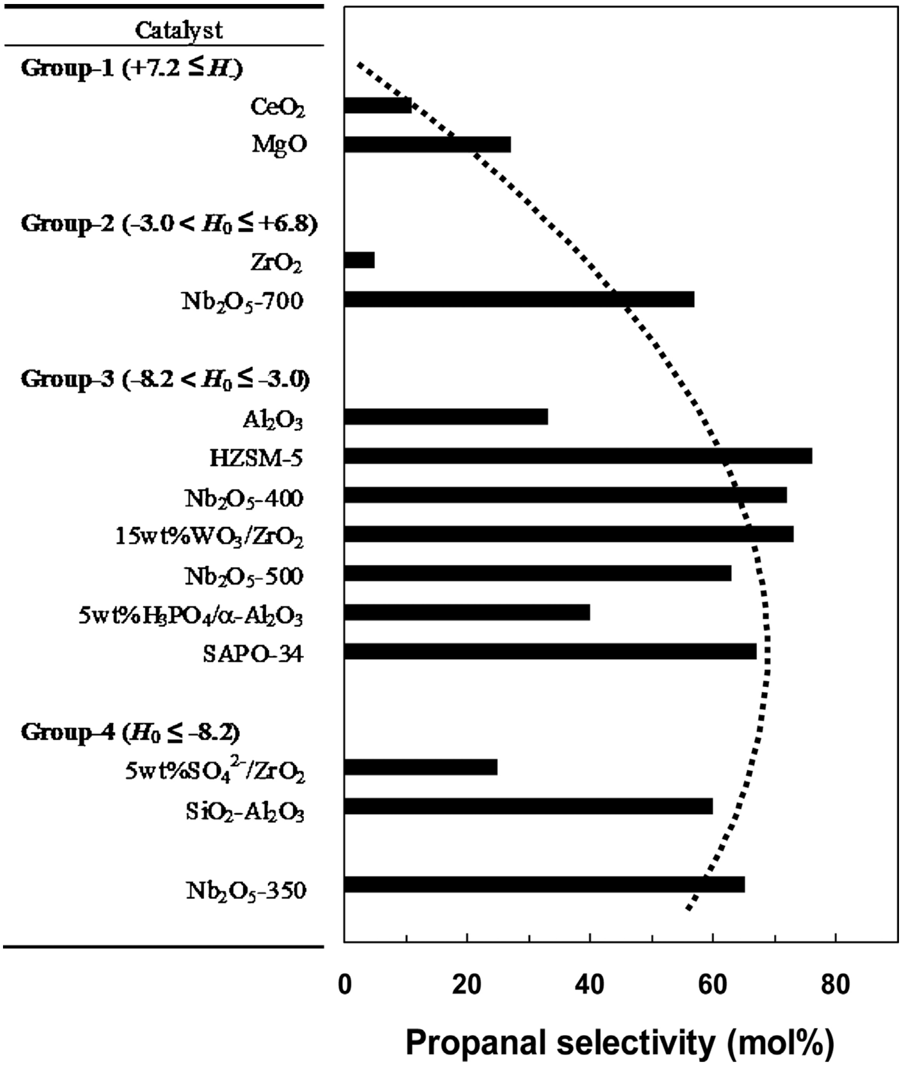

Fig. 1. Catalyst highest acid–base strength (H_0 or H_-) and propanal selectivity at 9–10 h in the dehydration of 1,2-PD.

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1,2-PD was higher than 60 mol% over the strongly acidic catalysts except Al_2O_3 and 5 wt% $H_3PO_4/\alpha\text{-}Al_2O_3$; the selectivity could even be higher than 70 mol% over HZSM-5, Nb_2O_5-400 and WO_3/ZrO_2. Therefore, the most favorable acidic sites for the intra-molecular dehydration of 1,2-PD to produce propanal would be those having acid strength at $-8.2 < H_0 \leq -3.0$. This dependence on the catalyst acid strength of propanal formation in the dehydration of 1,2-PD well resembles that of acrolein formation in the double dehydration of GL, with 5 wt% $H_3PO_4/\alpha\text{-}Al_2O_3$ catalyst as the only exceptional catalyst [20]. However, propanal selectivity up to 60–65 mol% was also obtained over two very strong acidic catalysts, SiO_2–Al_2O_3 and Nb_2O_5-350 in Group-4, which could be due to that these two catalysts had a higher fractional acidity at $-8.2 < H_0 \leq -3.0$ (> 50%, Table 2).

Fig. 2 correlates the catalyst mass-specific activity (the catalytic rates for 1,2-PD consumption and propanal production based on a unit catalyst mass) with the fractional acidity of the catalyst at $-8.2 < H_0 \leq -3.0$. It is clear that the catalyst mass-specific rates both for 1,2-PD consumption and propanal production tend to increase with the fractional acidity at $-8.2 < H_0 \leq -3.0$, suggesting again that the strongly acidic sites at $-8.2 < H_0 \leq -3.0$ are more efficient for propanal production than those of medium strong and weakly acidic sites. These correlations are essentially similar to earlier observations on ethanol production in catalytic ethylene hydration [37] and acrolein production in catalytic GL dehydration [20] over various solid acid catalysts.

Besides acid strength, the nature of acid sites (Brønsted or Lewis sits) would also influence the catalytic performance of the solid acid catalysts. Among the strongly acidic catalysts in Group-3, Al_2O_3 could be regarded as a typical Lewis acid catalyst [37]. This catalyst produced a poor selectivity (<40 mol%) for the formation of propanal. In contrast, the typical Brønsted acid HZSM-5 and those having Brønsted as well as Lewis acid sites, like WO_3/ZrO_2, Nb_2O_5-400 and -350, produced the highest propanal selectivity (72–76 mol%) for the dehydration of 1,2-PD. Thus, in consideration of the selectivity for propanal (the major product), Brønsted acid sites are superior to Lewis acid ones for the 1,2-PD dehydration reaction. This could be even more conclusive if during the reaction a possible in situ transformation of some Lewis acid sites into Brønsted ones was taken into account [38]; which could easily be

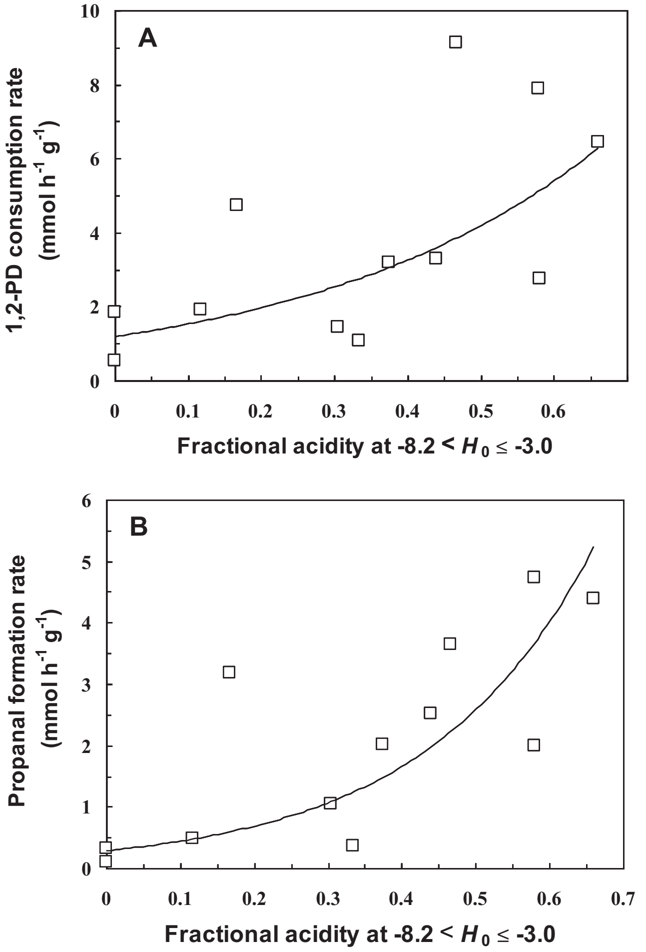

Fig. 2. Fractional acidity at $-8.2 < H_0 \leq -3.0$ of the investigated catalysts and their mass specific catalytic rates for 1,2-PD consumption (A) and propanal formation (B) at TOS = 9–10 h.

Table 5
Product distribution at 315 °C and 1,2-PD GHSV = 400 h^{-1} over solid acid–base catalysts.

Catalyst (0.63 mL)	X^a (%)	Product selectivity at TOS = 9–10 h (mol%)						Carbon deposits (mg g-cat^{-1})
		Propanal	Acetaldehyde	Acetone	1-Propanol	Allylalcohol	Unknowns[b]	
Group-1								
CeO_2	22	11	2	16	9	1	61[c]	2.9
MgO	10	27	2	26	4	2	39	7.5
Group-2								
ZrO_2	65	5	0	5	20	2	68	38.3
Nb_2O_5-700	20	57	3	5	6	4	25	1.6
Group-3								
Al_2O_3	92	40	2	8	15	1	34	41.6
HZSM-5	55	76	0	6	7	3	8	29.2
Nb_2O_5-400	69	72	0	6	1	2	19	74.0
15 wt% WO_3/ZrO_2	45	73	1	5	3	1	17	–
Nb_2O_5-500	85	63	0	7	6	2	22	33.7
5 wt% $H_3PO_4/\alpha\text{-}Al_2O_3$	30	33	1	13	15	5	33	1.6
SAPO-34	83	67	0	6	6	1	20	75.6
Group-4								
5 wt% SO_4^{2-}/ZrO_2	60	25	2	3	16	0	54	-
SiO_2–Al_2O_3	69	60	2	4	7	1	26	38.4
Nb_2O_5-350	65	65	0	6	4	2	23	85.2

[a] Conversion of 1,2-PD.
[b] Selectivity for the unknowns (mol%) = 100 – total selectivity for all identified products, including the carbonaceous deposits formed during TOS = 9–10 h.
[c] Methanol (5 mol%) and ethanol (8 mol%), which were detected only when CeO_2 was the catalyst, were also included arbitrarily here as “unknowns”.

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Table 6
Product distribution at 315 °C and 1,3-PD GHSV = 400 h^{-1} over solid acid–base catalysts.

Catalyst (0.63 mL)	X^a (%)	Product selectivity at TOS = 9–10 h (mol%)						Carbon deposits (mg g-cat^{-1})
		Allylalcohol	Acetaldehyde	Propanal	Acrolein	1-Propanol	Unknowns^b	
Group-1								
CeO_2	50	91	0	2	1	2	4	3.3
MgO	13	8	18	4	20	2	48	9.0
Group-2								
ZrO_2	17	33	4	12	15	15	21	–
Nb_2O_5-700	5	7	0	2	16	14	61	2.2
Group-3								
Al_2O_3	42	16	5	9	18	11	41	–
HZSM-5	11	11	0	11	15	9	54	23.2
15 wt% WO_3/ZrO_2	20	11	1	35	12	4	37	–
5 wt% H_3PO_4/α-Al_2O_3	4	11	0	4	7	2	76	1.0
SAPO-34	8	10	0	4	5	2	79	150.4
Group-4								
SiO_2–Al_2O_3	47	12	4	17	20	14	33	–
Hβ	12	16	1	10	22	17	34	–
Nb_2O_5-350	48	20	1	10	10	6	53	45.5

[a] Conversion of 1,3-PD.
[b] Selectivity for the unknowns (mol%) = 100 – total selectivity for all identified products.

promoted by the presence of a large amount of water in the reaction feed (molar H_2O-to-1,2-PD ratio was 9). However, the selectivity for propanal was surprisingly low (33 mol%) over 5 wt% H_3PO_4/α-Al_2O_3, a typical supported Brønsted acid catalyst, which is the only case outside the generality. This exception could arise from a partial "dissolution" into the reaction stream of H_3PO_4 from the catalyst surface, probably during the early stage of the reaction.

3.2. Catalytic dehydration of 1,3-PD

Table 6 presents the reactant conversion and product distribution data from the catalytic dehydration of 1,3-PD at TOS = 9–10 h. The identified products include allyl alcohol, propanal, acrolein and 1-propanol. However, these products constituted 20–80% of all of the reaction products except when CeO_2 was the catalyst; the others remained unidentified and were denoted as unknown in the table. Apparently, the dehydration reaction of 1,3-PD over the acid–base catalysts other than CeO_2 produced very scattered products; no catalyst except CeO_2 was found able to offer a product with a selectivity higher than 35 mol%. It should be mentioned that acrolein, which was not detected in the products of 1,2-PD dehydration, was produced with a low selectivity (2–20 mol%) in the dehydration of 1,3-PD. The very exceptional CeO_2 catalyst effected a distinctly high selectivity (ca. 90 mol%) for the formation of allyl alcohol. This specific feature of the CeO_2 catalyst agrees with the observation of Sato et al. [31,32], who obtained a selectivity as high as 98 mol% for the formation of allyl alcohol from the dehydration of aqueous 1,3-PD at 325 °C over their CeO_2 catalyst. A redox catalysis was proposed based on inter-conversion between Ce^{4+} and Ce^{3+} ions at the surface of CeO_2 [31], the detail of which remained to be disclosed in further investigation.

The very scattered product distribution over the acid–base catalysts other than CeO_2 indicates that there is no clear relationship between the product selectivity and the catalyst acid–base property in the catalytic dehydration of 1,3-PD. This is very different from the catalytic dehydration reactions of 1,2-PD presented above and GL in our earlier work [21], where the surface acidic sites with acidity of $-8.2 < H_0 \leq -3.0$ seem to be responsible for the selective formation of propanal from 1,2-PD and acrolein from GL. On the other hand, the conversion levels of 1,3-PD over the acidic catalysts in Table 6 are distinctly lower than those of 1,2-PD in Table 5, revealing that the reactivity of 1,3-PD, which has no secondary OH or hydroxyl group bonded with the central carbon atom, is much lower than 1,2-PD over the acidic catalysts. However, the reactivity (conversion) of 1,3-PD became much higher than that of 1,2-PD when the basic CeO_2 and MgO were used as the catalyst (Tables 3 and 4).

3.3. Reaction channels of propane polyols over acid–base catalysts

Scheme 1 presents the possible reaction channels of 1,2-PD based on the products identified during the catalytic gas-phase dehydration of aqueous 1,2-PD (Table 5). A dehydration by elimination of the OH on the secondary carbon atoms of 1,2-PD molecules would result in formation of 1-hydroxy-1-propene (Channel ***I***) or allyl alcohol (Channel ***II***). The former molecule is unstable and can easily undergo a rapid rearrangement leading to propanal. The other dehydration channel would be initiated by eliminating the OH on the primary carbon atoms, which gives 2-hydroxy-1-propene as an unstable intermediate and acetone as the final product (Channel ***III***). The high selectivity of propanal in the products of 1,2-PD (Table 5) demonstrates that the major reaction channel for the dehydration of aqueous 1,2-PD is the one initiated by elimination of the OH at the secondary carbon atom, followed by a proton-abstraction from the terminal carbon bonded with the other OH (Channel ***I***). The reaction channels leading to allyl alcohol (Channel ***II***) and acetone (Channel ***III***) are of minor importance. It is therefore that the dehydration of 1,2-PD proceeds mainly by an acid-catalyzed E1 mechanism [37], with which a secondary carbenium ion would form according to Channel ***I*** but a primary carbenium ion according to Channel ***III***. That is why propanal from Channel ***I*** was always far more than acetone from Channel ***III*** over the acid catalysts as the secondary carbenium ions are more stable than the primary carbenium ions. The formation of allyl alcohol would also go through the secondary carbenium ion (Channel ***II***), however, the follow up proton-abstraction from the terminal methyl (CH_3) would be much more difficult than from the terminal hydroxyl methene (CH_2OH) because of the electron withdrawing character of OH; this would account for the low visibility of allyl alcohol in the dehydration product of 1,2-PD.

Our detected formation of formaldehyde and acetaldehyde suggests that another reaction channel would also be involved during the reaction of 1,2-PD, that would be a hydrogenolysis channel which yields acetaldehyde and formaldehyde (Channel ***IV*** in Scheme 1). The other by-products, like 1-propanol, ethanol and methanol, would come from secondary hydrogenation reactions

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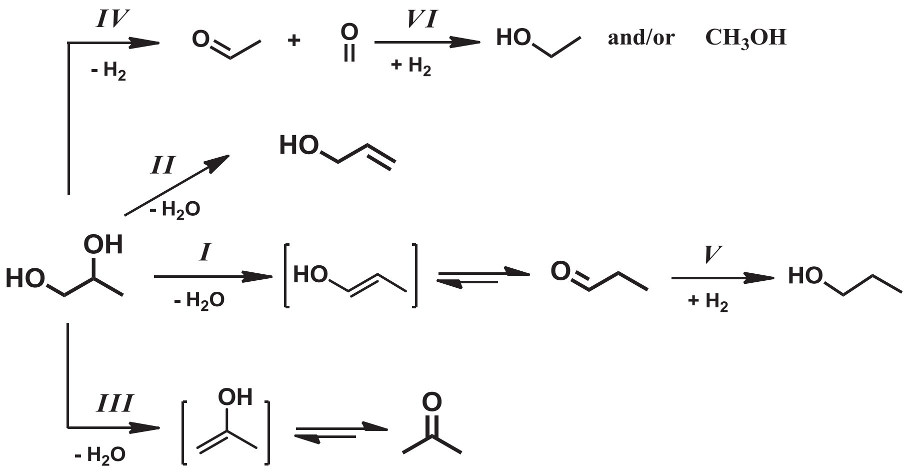


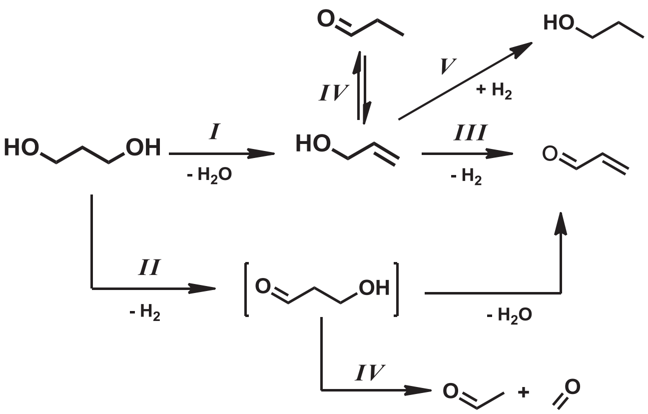
Scheme 1. Reactions involved in 1,2-PD dehydration over solid acid–base catalysts.

of those primary aldehyde products (Channels ***V*** and ***VI***). Hydrogen required for these secondary reactions would be produced from those reactions leading to unidentified heavier products and/or carbonaceous deposits on the catalyst surfaces. Such hydrogenation/dehydrogenation reactions would be concerned with the involvement of surface basic sites, as shown in particular by the formation of methanol (5 mol%) and ethanol (8 mol%) over the basic CeO_2 catalyst.

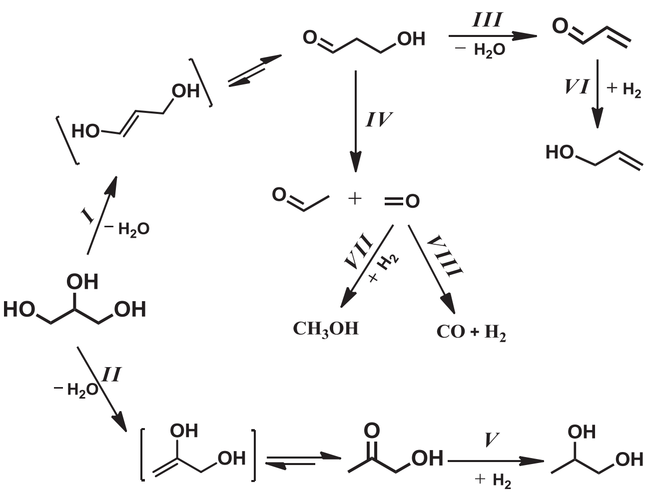
Scheme 2 shows the possible reaction channels of 1,3-PD based on the products identified during the catalytic gas-phase dehydration of aqueous 1,3-PD (Table 6). The dehydration by elimination of the OH at either terminal CH_2OH (Channel ***I***) would lead to the formation of allyl alcohol. This reaction channel is clearly demonstrated by the very high selectivity (>90 mol%) for allyl alcohol obtained over CeO_2 catalyst, either here in this study or in the earlier literature [31,32], although the selectivity for allyl alcohol was always lower than 33 mol% over the other catalysts investigated in this study. The other reaction channel of 1,3-PD is not dehydration but dehydrogenation to give 3-hydroxyl propanal, a very reactive intermediate that can easily undergo dehydration to produce acrolein (Channel ***II***). Also, a secondary dehydrogenation reaction of the allyl alcohol, the primary product of Channel ***I***, would also result in formation of acrolein (Channel ***III***). Other secondary reactions for this primary allyl alcohol include isomerization to form propanal (Channel ***IV***) and hydrogenation to give 1-propanol (Channel ***V***). Another exit of the very reactive intermediate in Channel ***II*** (i.e., 3-hydroxy propanal) would be its decomposition to give acetaldehyde and formaldehyde, probably according to a reverse aldol condensation mechanism (Channel ***VI***).

It would be of interest to compare the reaction channels for the gas-phase dehydration of 1,2- and 1,3-PD with those of aqueous GL observed in our earlier work, as shown in Scheme 3 [20]. The main reaction channel for 1.2-PD and GL is the dehydration by eliminating the secondary OH group (at the central carbon atom), resulting in propanal from 1,2-PD and acrolein from GL. This would be the mechanistic basis for the similar dependences on the catalyst acidity of the selectivity for propanal from 1,2-PD dehydration and for acrolein from GL dehydration. Interestingly, the highest selectivity for propanl (70–75 mol%) from aqueous 1,2-PD obtained in this work is also close to that of acrolein from aqueous GL in our earlier work [20–22,39]. These similarities would probably arise from the presence of two adjacent hydroxyls in the structures of 1,2-PD and GL molecules.

The absence of a secondary OH group in 1,3-PD would be responsible for its quite different reactivity and scattered products from those of 1,2-PD and GL over the acid–base catalysts. Though the key reactive intermediate, 3-hydroxyl propanal, of the main reaction channel for the catalytic dehydration of GL (Channel ***I*** in Scheme 3) could also be proposed as a possible reaction channel for the reaction of aqueous 1,3-PD (Channel ***II*** in Scheme 2), the reaction leading to this intermediate from 1,3-PD was rather dehydration but dehydrogenation. The very scattered products detected in the reaction of aqueous 1,3-PD (Table 6) would hint that the



Scheme 2. Reactions involved in 1,3-PD dehydration over solid acid–base catalysts.



Scheme 3. Reactions involved in GL dehydration over solid acid–base catalysts [20].

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dehydrogenation channel leading to this very reactive 3-hydroxyl propanal (Channel ***II*** in Scheme 2) was not favorable in competing with the dehydration channel leading to allyl alcohol (Channel ***I*** in Scheme 2). On the catalysts other than CeO_2, allyl alcohol seems highly reactive to give secondary products like acrolein, propanal, 1-propanol (Channels ***III***, ***IV*** and ***V*** in Scheme 2).

It deserves to mention that this work is motivated to uncover the similarity/dissimilarity between the reactivity and product selectivity of the three propane polyols over solid acid–base catalysts. The above discussion makes no attempt to discriminate between acid and base catalysts from acid–base bifunctional ones though several samples in Tables 5 and 6 (e.g., ZrO_2, CeO_2 and Al_2O_3) were already known to be more or less bifunctional [37]. ZrO_2 had proven a typical weakly acidic and weakly basic catalyst because of its unique catalytic selectivity in a number of reactions [37] and its capability to chemisorb both basic (NH_3) and acidic (CO_2 or SO_2) probes with comparable heats of adsorption [40,41] or desorption temperatures [42]. In this present work, Al_2O_3 appears as a better solid acid and CeO_2 a better base than an acid–base bifuntional solid if one would judge by the selectivity for propanal in the reaction of 1,2-PD (Table 5 and Fig. 1) and for allyl alcohol in the reaction 1,3-PD (Table 6). Two model reactions in earlier literature, dehydration of 2-butanol [43] and deamination of 2-butylamine [44], had also demonstrated that Al_2O_3 is a better solid acid than ZrO_2; both reactions gave 2-butenes as the dominant product over Al_2O_3 but 1-butene over the acid–base bifunctional ZrO_2. If we could put the unknown products aside, the bifunctionality of ZrO_2 would be characterized by showing a higher selectivity for 1-propanol in the reaction of 1,2-PD (Table 5), and for acrolein and 1-propanol in the reaction of 1,3-PD (Table 6), featuring a unique property of ZrO_2 [37] for promoting secondary hydrogenation reactions of the primary propanal (Scheme 1) or allyl alcohol (Scheme 2). When the hydrogenated product(s) were added to propanal in the reaction of 1,2-PD or to allyl alcohol in the reaction of 1,3-PD, ZrO_2 would stand just in between the more basic CeO_2 and more acidic Al_2O_3.

The correlations shown in Figs. 1 and 2 emphasize therefore the importance of surface acid strength on the catalytic reactivity and selectivity without consideration of the effects of co-presence of acidic and basic sites [30,39–41,44] and their surface densities [39,44] on the solid catalysts. Also, no clear information on the nature of the unknown products and carbonaceous deposits could violate more or less the correlations. However, the present data seem enough to roughly reach the ultimate purpose to uncover the dependence on the catalyst acidity of the reactivity and product selectivity of the three propane polyols, which points to that the reactions of 1,2-PD and GL were both initiated by activation of their secondary hydroxyl groups.

4. Conclusions

This work demonstrates that the dependences on the catalyst acidity of the gas-phase dehydration reactions of aqueous GL and 1,2-PD are very different from that of aqueous 1,3-PD. Fairly high selectivity (40–75 mol%) for propanal formation from 1,2-PD was obtained over those catalysts having fairly high fractional acidity at $-8.2 < H_0 \leq -3.0$, which resembles the formation of acrolein from GL over the same catalysts. On the other hand, the catalytic dehydration of aqueous 1,3-PD gave very scattered products over the investigated catalysts; no catalyst except CeO_2 was able to offer a product with a selectivity higher than 35 mol%. These similarity and dissimilarity between the catalytic dehydration of the three propane polyol molecules are discussed based on the selectivity of the identified main products and their dependences on the catalyst acidity. Mechanistic consideration for the similar dependences on the catalyst acidity of the selectivity for propanal formation from 1,2-PD and for acrolein production from GL is given.

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