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Comparison of kinetics and reaction pathways for hydrodeoxygenation of C_3 alcohols on $\mathsf{Pt}/\mathsf{Al}_2\mathsf{O}_3$

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1. Introduction

Selective conversion of biomass resources such as polysaccharides [1,2], lignin [3,4], bio-ethanol, and glycerol [5–11] requires highly efficient catalysts. Within these biomass feedstocks, glycerol is a very attractive option due to its relatively low cost and wide availability as a by-product of bio-diesel production. It is considered to be, therefore, one of the top 12 building block chemicals of a biorefinery process [12].

Glycerol can be either converted to high value-added oxygenated chemicals such as propanediols via hydrodeoxygenation, or can be used to produce hydrogen through aqueous phase reforming process. The aqueous phase deoxygenation of glycerol to propanediols requires selectively cleaving one of the C–O bonds, but preserving the C–C bonds. It occurs catalytically on dual functional catalysts via consecutive dehydration and hydrogenation in the presence of H₂ at moderate temperatures (453–543 K) and relatively high pressures (20–150 bar) [13–17]. On the other hand, the parallel route of aqueous phase reforming (APR) also occurs at identical conditions used for hydrodeoxygenation of alcohols [9–11]. The bifunctional catalyst Pt supported on Al_2O_3 , which had

ABSTRACT

The catalytic hydrodeoxygenation of C₃ alcohols (1- and 2-propanol, 1,2- and 1,3-propanediol, and glycerol) on Pt/Al₂O₃ has been mechanistically explored in the aqueous phase. Dehydrogenation on Pt and dehydration on alumina are the main elementary reaction pathways. In water, carbon–carbon bond cleavage for alcohols with terminal hydroxyl groups occurs via decarbonylation of aldehydes (generated by dehydrogenation of alcohols) and decarboxylation of acids, the latter being formed by disproportionation from aldehydes. The presence of water as solvent suppresses the dehydration for mono-alcohols mainly via blocking of Lewis acid sites by water. Dehydration is still the dominating primary reaction for 1,3-propanediol and glycerol, as the higher number of hydroxyl groups weakens the C–O bond strength. The overall reactivity of C₃ alcohols decreases in the order of 1,3-propanediol \approx glycerol > 1,2-propanediol \approx 1-propanol.

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potential hydrodeoxygenation ability on alcohols and exhibited exceeding 90% hydrogen selectivity from APR of alcohols [18,19], was selected in this work.

The competing pathways of aqueous phase hydrodeoxygenation and reforming have been extensively explored by Dumesic [9–11], Davis [20,21], Tomishige [14,22], and ourselves [23]. The key feature in determining the selectivity is the way and the extent of C–C and C–O bond cleavage. The pathway for C–O bond cleavage was suggested to occur either through dehydrogenation to form surface adsorbed species followed by direct cleavage catalyzed by metallic sites or via dehydration reactions catalyzed by acid sites associated with catalyst support [9]. The mechanism for C–C bond cleavage in aqueous phase reforming of alcohols producing smaller alkanes, CO_2 , and H_2 has not been unequivocally explained. While, the C–C bonds in alcohols were speculated to be cleaved by the metal catalyzed direct hydrogenolysis [9,18], we showed first evidence in a recent paper that direct hydrogenolytic cleavage of C–C bonds does not occur [23].

In the present paper, the kinetics in the catalytic conversion of C_3 alcohol molecules with different position of the hydroxyl group and number of hydroxyl groups (mono-alcohols, i.e., 1-propanol and 2-propanol; diols, i.e., 1,2-propanediol and 1,3-propanediol; and triol, i.e., glycerol) were systematically studied over Pt/Al₂O₃ in order to elucidate the reaction pathways and fundamental chemistry that lead to the C–C and C–O bond cleavage in the aqueous phase alcohol transformation. In addition, the different activity performances of 2-propanol in the gas phase and in the aqueous phase over Pt/Al₂O₃



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have also been compared to elucidate specific effects of the aqueous environment.

2. Experimental

2.1. Catalysts preparation

The 3 wt.% Pt/Al₂O₃ catalyst was prepared by the incipient wetness impregnation method, with platinum(II)-ammonium nitrate ([Pt(NH₃)₄](NO₃)₂, Strem chemicals) as precursor and γ -Al₂O₃ (Aeroxide Alu C-Degussa, specific surface area: 105 m²/g) as carrier. After impregnating the carrier with the aqueous solution of Pt precursor at ambient temperature, the catalyst was dried in air at 393 K for 12 h and calcined in synthetic air for 2 h at 673 K. Prior to the reaction and characterization, the catalyst was reduced in H₂ at 573 K for 2 h.

2.2. Catalyst characterization

Atomic absorption spectroscopy (AAS) was used for analyzing the metal loading. The nitrogen adsorption-desorption was adopted for measuring BET surface area and pore size distribution. The fraction of accessible Pt atoms was detected by hydrogen chemisorption. The temperature programmed desorption (TPD) of ammonia and carbon dioxide was used for acid and basic sites measuring. The characterization methods have been described in detail in a previous publication [23].

2.3. Catalyzed reactions

2.3.1. Gas phase reaction

The dehydrogenation/dehydration of 2-propanol was performed in a continuous fixed bed flow reactor at atmospheric pressure and temperature ranging from 393 to 523 K. The quartz tubular reactor (4 mm diameter) was packed with 20 mg catalyst diluted in 100 mg SiC. After the catalyst activation in H₂ at 573 K for 2 h, the reaction was performed by introducing a H₂ flow saturated with 2-propanol at 286.2 K (the 2-propanol partial pressure was 25 mbar) into the reactor. The effluent products were analyzed by a gas chromatography equipped with FID detector and Supelco-Wax column.

2.3.2. Aqueous phase reaction

Experiments with 1-propanol, 2-propanol, 1,2-propanediol, 1,3propanediol, and glycerol were conducted in a 300 ml batch autoclave (Parr Instrument). The reactants and the catalyst loaded in a closed glass vial were charged into the reactor, and then the reactor was purged with N2, which was also used as internal standard for vapor phase products analysis. When the required temperature and pressure were reached, the reaction was started after breaking the glass vial by stirring. The vapor phase was analyzed online by a gas chromatograph with TCD detector and two capillary columns (MS-5A and HP-Plot Q). Liquid samples were manually collected during the run and analyzed in a gas chromatograph equipped with an FID detector and a CP-Wax 57CB column. Typical reactions were conducted under the following conditions: 473 K, 40 bar total pressure of H₂, 100 g of 10 wt.% reactant aqueous solution, 0.3 g of 3 wt.% Pt/Al₂O₃, and 600 rpm stirring speed. All results were calculated and reported based on carbon basis.

2.4. Equilibrium and CO₂ solubility calculation

The reaction equilibrium compositions were calculated using the HSC software. Under reaction temperature and pressure, CO_2 would be produced and partially dissolved in water. This part of CO_2 cannot be detected by gas chromatograph, but needs to be considered for an accurate analysis. The solubility of CO₂ in water was, therefore, calculated according to the published literature [24]. At 473 K and a relatively low CO₂ partial pressure, the solubility of CO₂ in water approximately equals to $10^{-2} * p_{CO_2}$ (mol/kg water, p_{CO_2} in unit of bar).

3. Results and discussion

3.1. Catalysts characterization

The physicochemical properties of the 3 wt.% Pt/Al_2O_3 are summarized in Table 1. The BET specific surface area was 88 m²/g, while the dispersion of Pt was 90%. The acid and base site concentrations of 3 wt.% Pt/Al_2O_3 were 0.160 and 0.015 mmol/g, respectively. It should be noted that the acid-base properties only represent the starting catalyst, as the alumina support transforms during the reaction under hydrothermal environment into aluminum hydroxide (Böhmite).

3.2. Conversion of 2-propanol on Pt/Al₂O₃ in the gas phase

In order to compare the catalytic conversion of an alcohol at the gas-solid interface with the conversion at the aqueous-solid interface, we firstly explored the reactions of 2-propanol on Pt/Al_2O_3 in the gas phase. It is known that the catalyst acidity is related to its ability to dehydrate 2-propanol to propene, while its dehydrogenation to acetone is catalyzed by a catalytic function that is able to abstract a proton by a strong basic site and the hydride anion by a Lewis acid site or a metal function [25,26]. The results of 2-propanol conversion over $3 \text{ wt.\% Pt}/Al_2O_3$ at 1 bar in the gas phase are shown in Fig. 1.

It shows that the dehydrogenation and dehydration competed over the whole conversion range. Dehydrogenation of 2-propanol to acetone over $3 \text{ wt.\% Pt/Al}_2O_3$ was the dominating reaction at relatively low temperatures (below 473 K), while propane formed via consecutive dehydration and hydrogenation became the major product at higher temperatures. In addition, pure Al₂O₃ selectively dehydrated of 2-propanol to propene at identical conditions. Therefore, it can be concluded that dehydration was catalyzed by the Lewis acid sites of Al₂O₃ (reaction rate at 473 K: 69.0 mmol s⁻¹ mol_{acid site}⁻¹) and Pt was responsible for the dehydrogenation (reaction rate at 473 K: 96.0 mmol s⁻¹ mol_{Pt-surf atom}⁻¹). The apparent activation energies for dehydration and dehydrogenation of 2-propanol over $3 \text{ wt.\% Pt/Al}_2O_3$ were 71 and 44 kJ/mol, respectively.



Fig. 1. Conversion of 2-propanol (\blacklozenge) and yield of acetone (\blacksquare) and propane (\blacktriangle) as a function of temperature on 3 wt.% Pt/Al₂O₃ in gas phase reaction. (Reaction conditions: 3 wt.% Pt/Al₂O₃ 20 mg, 2-propanol partial pressure 25 mbar, H₂ flow 40 ml/min.)

Table 1	
Physicochemical properties of Pt/Al ₂ O ₃ catalys	st.

Catalyst	Pt loading	Surface	Dispersion	Acidity	Basicity
	(wt.%)	area (m²/g)	(H/Pt)	(mmolNH3/g)	(mmolCO ₂ /g)
Pt/Al ₂ O ₃	2.93	88	0.90	0.16	0.015

3.3. Conversion of 2-propanol on Pt/Al_2O_3 in the aqueous phase

The dehydrogenation to acetone was the dominating primary reaction of the conversion of 2-propanol on Pt/Al₂O₃ at 473 K in the aqueous phase (see Fig. 2). The initial rate of dehydrogenation (48.0 mmol s⁻¹ mol_{Pt-surf atom}⁻¹) was reduced to 50% of the rate found in the gas phase (96.0 mmol s⁻¹ mol_{Pt-surf atom}⁻¹). As the hydrogen concentration (0.023 mol/L, calculated from the solubility of hydrogen in water [27]) in aqueous phase reaction is comparable with that in the gas phase reaction (0.026 mol/L), the activity coefficient of hydrogen is close to one. We speculate that the slower dehydrogenation rate in aqueous phase is, therefore, mainly related to the competitive adsorption of water and 2-propanol on Pt active sites. Only a small fraction was converted to propane, presumably via the slow dehydration of the alcohol on the Al₂O₃ support (initial rate: 0.4 mmol s⁻¹ mol_{acid site}⁻¹) and the following hydrogenation on Pt.

It is important to note that the dehydration rate of 2-propanol in the aqueous phase was two orders of magnitude slower than that in the gas phase (see Table 2). This could be attributed either to the decrease in Lewis acidity caused by the transformation of γ -Al₂O₃ to aluminum hydroxide (Böhmite) [28,29], or to the fact that water essentially blocks the Lewis acid sites active in dehydrating 2-propanol in the gas phase. As it has been established that the transformation of γ -Al₂O₃ in water is a relatively slow process [29], and the decrease of 2-propanol dehydration rate is substantial even at initial time when alumina is still not measurably converted, we conclude the drastic activity change of Pt/Al₂O₃ in aqueous solution is mainly caused by the competitive adsorption of water on Lewis acid sites.

Experiments with pure γ -Al₂O₃ showed a significantly lower conversion, which confirmed again that Pt is essential for 2propanol dehydrogenation. It is noted that the potential products of C–C or C–O bond cleavage from 2-propanol were not observed, suggesting that Pt/Al₂O₃ is not able to cleave these bonds in 2propanol under the reaction conditions. It shows unequivocally that hydrogenolysis reactions do not occur.

3.4. Aqueous phase conversion of 1-propanol

The products of 1-propanol conversion versus reaction time over 3 wt.% Pt/Al₂O₃ are plotted in Fig. 3. In contrast to 2-propanol conversion, the reaction of 1-propanol mainly led to CO₂ and ethane (initial rate: 1.1 mmol s⁻¹ mol_{Pt-surf atom}⁻¹). The ratio of ethane to CO₂ was approximately 2.0 based on carbon basis. The presence of H₂ (cannot be detected in H₂ atmosphere) is inferred from the reaction stoichiometry. Similar to the reaction of 2-propanol, only small amounts of propane (not shown at here) were formed from the C₃ alcohol dehydration–hydrogenation on Al₂O₃. The dehydration rate of 1-propanol (0.3 mmol s⁻¹ mol_{acid site}⁻¹) was slightly lower than the rate of 2-propanol (0.4 mmol s⁻¹ mol_{acid site}⁻¹) (see Table 2), which is in agreement with the literature [30] that the secondary hydroxyl group exhibits higher dehydration activity than the primary hydroxyl group.

Propanal was only observed in traces (concentration < 0.02%), which suggests rapid decarbonylation to ethane and CO or disproportionation of the formed propanal to propanol and propionic acid followed by decarboxylation to ethane and CO₂. Propanal and propionic acid were clearly detected as reaction intermediates in relatively large amounts for 1-propanol conversion in the absence of hydrogen [23]. The direct pathway of hydrogenolysis of 1propanol can be excluded, as the C–C bond strengths in 1-propanol and 2-propanol are quite similar (see Table 3, i.e., 357 kJ/mol for 1-propanol and 368 kJ/mol for 2-propanol). This indicates that the formation of hydrogen, ethane, and CO₂ follows a reaction pathway characterized by dehydrogenation, decarbonylation (–CO) or disproportionation (Tishchenko or Cannizzaro type reactions), and decarboxylation (–CO₂).

At present, it is not possible to differentiate between these two latter mechanisms (Tishchenko or Cannizzaro) for the disproportionation of aldehyde into an acid and an alcohol. The Tishchenko reaction is catalyzed by acid catalysts, and an ester (propylpropionate) is formed in the first step, which is subsequently rapidly hydrolyzed at the current reaction conditions. On the other hand, the occurrence of Cannizzaro reaction requires basic sites of the catalysts, and it can be strongly enhanced by transition metals [32]. Both disproportionation pathways are possible with Pt/Al₂O₃, as the Böhmite compound contains both acid and base sites.





Fig. 3. Yield of ethane (\blacksquare), carbon dioxide (\blacktriangle) on conversion of 1-propanol over 3 wt.% Pt/Al₂O₃ as a function of time in aqueous solution. (Experimental conditions: *T* = 473 K, total pressure 40 bar, 1-propanol concentration 10 wt.%.)



Table 2

Comparison of reaction rates for conversion of C_3 alcohols in aqu	leous phase at 473 K.
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	Reaction pathways, products and reaction rates			
Reactants	Dehydrogenation (mmol s ⁻¹ mol _{Pt-surf atom} ⁻¹)	Dehydration (mmol s ⁻¹ mol _{acid site} ⁻¹)	$\begin{array}{l} Decarbonylation/decarboxylation \\ (mmols^{-1}mol_{Pt-surfatom}{}^{-1}) \end{array}$	
2-Propanol ^a	96.0 ^b	69.0	-	
	Acetone	Propane	-	
2-Propanol	48.0 ^b	0.4	-	
	Acetone	Propane	-	
1-Propanol	-	0.3	1.1*	
	-	Propane	Ethane, CO ₂	
1,2-Propanediol	8.5 ^b	0.2	1.0	
	Hydroxyacetone	1-Propanol, 2-propanol	Ethanol, methane, CO ₂	
1,3-Propanediol	-	11.5 ^b	1.0	
	-	1-Propanol	Ethanol, ethane, CO ₂	
Glycerol	-	4.6 ^b	1.4	
	-	Hydroxyacetone,	Ethylene glycol, ethanol,	
		1,2-propanediol	methanol, CO ₂	

^a Reaction performed under gas phase.

^b Primary reaction pathway and main products.

Table 3

C-C and C-O bond energies in C₃ alcohols [31].

Compounds	1-Propanol	2-Propanol	1,2-Propanediol	Glycerol	Glycerol
Structure	$C_2H_5CH_2$ —OH	OH CH ₃ -CH-CH ₃	OH OH CH ₃ -CH-CH ₂	OH OH OH 	OH OH OH CH ₂ -CH-CH ₂
C–O bond energy (kJ/mol)	392.0	397.9 OH	- 0H 0H	335.6 OH OH OH	333.0
Structure	C_2H_5 — CH_2OH	CH ₃ —CH-CH ₃	CH ₃ -CH—CH ₂	 CH ₂ -CH—CH ₂	
C–C bond energy (kJ/mol)	356.9	367.8	358.9	347.0	

In the potential route of propanal decarbonylation to ethane and CO, the produced CO is converted further to CO_2 and hydrogen through the water gas shift reaction. It has been observed that the concentration of CO in the products was slightly higher (0.015 C%) than the expected equilibrium value (0.007 C%, calculated from the observed CO_2 concentration). Therefore, it can be concluded that the parallel reaction of decarbonylation also contributes to 1-propanol conversion. However, quantitative differentiation between the reaction pathways of disproportionation followed by decarboxylation of the acid and decarbonylation followed by water gas shift is not attempted here.

3.5. Aqueous phase conversion of 1,2- and 1,3-propanediols

The reactions of 1,2-propanediol having a primary and a secondary hydroxyl group, and 1,3-propanediol with two primary hydroxyl groups were studied at identical reaction conditions (see Figs. 4 and 5). Hydroxyacetone, ethanol, and CO₂ were the main products of 1,2-propanediol conversion, and small amounts of 1-propanol, 2-propanol, and methane were also formed. The yield of hydroxyacetone formed through dehydrogenation of 1,2propanediol (initial rate: 8.5 mmol s⁻¹ mol_{Pt-surf atom}⁻¹) rapidly reached a constant value, which is determined by the high hydrogen pressure limiting further conversion.

Because the direct hydrogenolysis of C–C bonds of propanol does not occur under the present reaction conditions (see above), and the C–C bond strengths of 1,2-propanediol (359 kJ/mol) is quite close to that of propanol (357 kJ/mol) (see Table 3), ethanol and CO₂ are concluded to be formed via decarbonylation or decarboxylation (initial rate: $1.0 \text{ mmol s}^{-1} \text{ mol}_{Pt-surf atom}^{-1}$). For the reaction pathway, 1,2propanediol is dehydrogenated to 2-hydroxypropionaldehyde (not detected due to its high reactivity), which is either instantly decarbonylated to ethanol and CO followed by water gas shift reaction, or rapidly converted to 1,2-propanediol and 2-hydroxypropanoic acid via Tishchenko/Cannizzaro type disproportionation followed by decarboxylation of the acid, leading to ethanol and CO₂.

The formation rate of ethanol decreased slightly, while the formation rate of CO_2 increased moderately with the reaction time, leading to a ratio of ethanol to CO_2 that is lower than the 2.0 on carbon basis expected for ideal stoichiometry. This indicates that ethanol underwent further reaction to methane and CO_2 via analogous reaction pathways as described above. If the converted ethanol was also taken into account, the initial ratio of ethanol to CO_2 (calculated by (ethanol + 2× methane)/(CO_2 -methane) according to stoichiometry) was very close to 2.0 on carbon basis, clarifying that ethanol is involved to some extent in decarboxylation



Fig. 4. Yield of hydroxyacetone (\blacklozenge), ethanol (\blacksquare), carbon dioxide (\blacktriangle), methane (\bigcirc), 1-propanol (\triangle), and 2-propanol (\square) on conversion of 1,2-propanediol over 3 wt.% Pt/Al₂O₃ as a function of time in aqueous solution. (Experimental conditions: *T*=473 K, total pressure 40 bar, 1,2-propanediol concentration 10 wt.%.)



Fig. 5. Products distribution for 1,3-propanediol conversion over $3 \text{ wt.\% Pt/Al}_2O_3$ in aqueous solution in the presence of H₂; 1-propanol (\bullet), ethanol (\bullet), carbon dioxide (\blacktriangle), ethane (\blacksquare). (Experimental conditions: *T*=473 K, total pressure 40 bar, 1,3-propanediol concentration 10 wt.%.)

or decarbonylation reactions. 1-Propanol and 2-propanol were produced through sequential dehydration–hydrogenation of 1,2-propanediol over Al_2O_3 (initial rate: $0.2 \text{ mmol s}^{-1} \text{ mol}_{acid site}^{-1}$), and the produced amount of 1-propanol was higher than that of 2-propanol, which is attributed to the higher dehydration activity of secondary hydroxyl group than that of the primary hydroxyl group.

The results of the conversion of 1,3-propanediol at 473 K and 40 bar hydrogen are compiled in Fig. 5. 1-Propanol was the main product at initial conversion. Ethane, ethanol, CO_2 , and trace amounts of propane, propanal, propionic acid, methane, and methanol were also observed.

1-Propanol is highly selectively produced through the dehydration of 1,3-propanediol (initial rate: 11.5 mmols⁻¹ mol_{acid site}⁻¹) and the subsequent hydrogenation, which then further undergoes the same reaction sequences of dehydrogenation, followed by either decarbonylation with a subsequent water gas shift reaction or disproportionation with a subsequent decarboxylation, leading to CO₂ and ethane. The observation of trace amounts of propanal and propionic acid provides strong evidence for this proposed decarbonylation and decarboxylation reaction pathway. CO₂ also can be produced directly from the starting reactant 1,3-propanediol via the parallel reaction pathway of dehydrogenation, decarbonylation and decarboxylation (initial rate: 1.0 mmol s^{-1} mol_{Pt-surf atom}⁻¹). The ratio of C₂ compounds (ethanol and ethane) to CO₂ is approximately 2.0 based on carbon basis, suggesting that CO₂ is produced through both reaction pathways. Propane is concluded to be formed via the dehydration of 1propanol. We speculate at present that methane is formed by the dehydrogenation, decarboxylation/decarbonylation of hydrogenation of CO₂.

3.6. Aqueous phase conversion of glycerol

The results of glycerol conversion in the aqueous phase at 473 K in the presence of H_2 (40 bar) are compiled in Fig. 6. Hydroxyacetone, 1,2-propanediol, ethylene glycol, ethanol, and CO₂ were the main products, and 1-propanol, 2-propanol, and methanol were formed in small concentrations.

1,2-Propanediol was selectively produced from glycerol (75% selectivity). It can be seen from Fig. 6 that the increase of 1,2-propanediol nearly equals the decrease of hydroxyacetone in selectivity as a function of time, suggesting that 1,2-propanediol is produced from the hydrogenation of hydroxyacetone. A control experiment with hydroxyacetone as reactant shows 98.5% selectivity to 1,2-propanediol under identical conditions, which



Fig. 6. Glycerol conversion over $3 \text{ wt.\% Pt/Al}_2O_3$ in the aqueous solution in the presence of H₂. 1,2-PD, 1,2-propanediol; acetol, hydroxyacetone; EG, ethylene glycol; EtOH, ethanol; others = 1-propanol + 2-propanol + methanol. (Experimental conditions: T = 473 K, total pressure 40 bar, glycerol concentration 10 wt.%.)

confirms the proposed reaction route. Therefore, the dehydration to hydroxyacetone is the dominating primary reaction step for glycerol conversion (initial rate: $4.6 \text{ mmol s}^{-1} \text{ mol}_{\text{acid site}}^{-1}$).

It is important to emphasize that all the other products appear to be formed along the same pathways as for other alcohols. Glyceraldehyde generated by dehydrogenation of glycerol is rapidly converted to ethylene glycol and CO₂, either through sequential decarbonylation and water gas shift reaction or via Tishchenko/Cannizzaro type disproportionation reactions over acid-base sites of Pt/Al₂O₃ followed by subsequent decarboxylation of glyceric acid. These intermediates were not detected, because their concentrations were very low due to their high reactivity and the equilibrium limitations caused by the high hydrogen pressure. Ethylene glycol can be further converted, either it is dehydrated to acetaldehvde, which in turn is hydrogenated to ethanol. or it is decomposed to CO₂ via dehydrogenation, disproportionation, and decarboxylation reactions (or decarbonylation reaction). The slight difference (5%) of C-C bond strengths in glycerol and propanols allows us to exclude direct hydrogenolysis for C-C bond cleavage pathway (see Table 3). 1-Propanol and 2-propanol were formed by subsequent conversion of propanediols along the pathways discussed above.

It is still not clear, if the acid sites active in the dehydration in water are of Brønsted or Lewis acid character. The strong absorption of water onto Lewis acid sites allows the conversion of Lewis acid sites to surface hydroxyl groups via rehydroxylation (or rehydration). This two-step rehydroxylation transformation involves nondissociative adsorption of H₂O on the Lewis acid sites followed by the subsequent dissociative chemisorption of H₂O and modification of the alumina surface [33,34]. Although the transformation is fairly rapid and thorough and so the concentration of exposed Lewis acid sites is limited. We speculate at present that weak Brønsted acid sites resulting e.g., from some isolated surface hydroxyl groups and identified by the shift of ν_{OH} on CO infrared adsorption [35], act as active sites for dehydration.

3.7. Summary of reaction pathways and reaction rates for aqueous phase conversion of C_3 alcohols over Pt/Al_2O_3

Summarizing the aqueous phase reactions with C₃ alcohols over Pt/Al₂O₃, dehydrogenation of alcohols to ketones on Pt is the main route for conversion of 2-propanol and 1,2-propanediol, and dehydration on alumina is the main route for conversion of 1,3propanediol and glycerol. It has been demonstrated that the direct hydrogenolysis of C–C and C–O bonds of the alcohols does not



Fig. 7. Proposed main reaction pathways for C–C bond cleavage in aqueous phase conversion of glycerol derived alcohols over Pt/Al₂O₃ (* either via Tishchenko or Cannizzaro type reactions).

take place over Pt/Al_2O_3 under the used reaction conditions. In comparison, the C–O bonds of C₃ alcohols are cleaved by dehydration reaction in the present work, while the C–C bonds of C₃ alcohols with terminal hydroxyl groups are cleaved by sequential dehydrogenation to aldehyde, followed by either disproportionation (Tishchenko or Cannizzaro type reactions) with a subsequent decarboxylation reaction, or decarbonylation with a subsequent water gas shift reaction (see Fig. 7).

The reaction rates of individual steps for C₃ alcohols conversion in aqueous phase are compiled in Table 2. For 2-propanol and 1,2propanediol conversion, dehydrogenation is the major step (initial rates: 48.0 and 8.5 mmol s⁻¹ mol_{Pt-surf atom}⁻¹, respectively), while dehydration is the minor reaction for mono-alcohols conversion with slow dehydration rates (i.e., 0.4 and 0.3 mmol s⁻¹ mol_{acid site}⁻¹ for 2-propanol and 1-propanol, respectively), which is mainly attributed to the blocking of Lewis acid sites by water.

Dehydration, however, is the dominating primary reaction for both 1,3-propanediol (initial rate: 11.5 mmol s⁻¹ mol_{acid site}⁻¹) and glycerol (initial rate: 4.6 mmol s⁻¹ mol_{acid site}⁻¹), with the dehydration rates being 10–40 times faster than that of mono-alcohols. We attribute this to the distinctly weaker C–O bond strengths with the increase of hydroxyl group number in alcohol molecule, e.g., 398 kJ/mol for 2-propanol and 333 kJ/mol for glycerol (see Table 3), which supposedly should lower the activation energies for 1,3-propanediol and glycerol dehydration compared with mono-alcohols. The C–C bond cleavage through decarbonylation and decarboxylation occurs at the C₃ alcohols with terminal hydroxyl groups and produces smaller alkanes and CO₂, attaining the comparable rates of ca. 1.0 mmol s⁻¹ mol_{Pt-surf atom}⁻¹. The overall reactivity decrease in the sequence of 1,3-propanediol (2.3 × 10⁻⁶ mol s⁻¹ g_{catalyst}⁻¹) ≈ glycerol (1.2 × 10⁻⁶ mol s⁻¹ g_{catalyst}⁻¹) ≈ 1-propanol (2.2 × 10⁻⁷ mol s⁻¹ g_{catalyst}⁻¹).

4. Conclusions

The catalytic conversion of 2-propanol at the gas-solid and aqueous-solid interfaces with Pt/Al_2O_3 shows that the rate of 2-propanol dehydration in the aqueous phase was two orders of magnitude slower than that in the gas phase. Because the catalytic dehydration in the gas phase is generally accepted to be initiated by OH^- abstraction from the alcohol, we conclude that this step is drastically retarded when the reaction is conducted in water. As γ -Al₂O₃ slowly transforms into aluminum hydroxide (Böhmite) under hydrothermal conditions, the weaker Lewis acidity due to rehydroxylation is possibly responsible for the rate decrease to some extent. However, the substantial decrease of 2-propanol dehydration rate even at initial conversion, when alumina is still not measurably converted, suggests that blocking of Lewis acid sites by the abundant water is the main reason leading to the drastic decrease of dehydration rate.

The C-O bonds of C₃ alcohols are cleaved by dehydration, while the C-C bonds of C₃ alcohols with terminal hydroxyl groups are cleaved by sequential dehydrogenation to aldehvde. followed by either disproportionation (Tishchenko or Cannizzaro type reactions) with a subsequent decarboxylation reaction, or decarbonylation with a subsequent water gas shift reaction. The presence of terminal hydroxyl group of alcohols is proved to be critical for C-C bond cleavage in this reaction sequence, as it allows forming the essential aldehyde intermediate, which opens the reaction pathway to decarbonylation and decarboxylation. The overall reaction rates decrease in the sequence of 1,3-propanediol \approx glycerol > 1,2-propanediol \approx 1-propanol, which depends on the number of hydroxyl groups in the molecule, as well as the number of primary hydroxyl groups. The higher concentration of the hydroxyl groups in one molecule weakens the C-O bond strengths, leading to higher dehydration rates.

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