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# A DRIFTS Study of Catalyzed Dehydration of Alcohols by Alumina-supported Heteropoly Acid

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**Abstract** Selectively catalyzed dehydration of ethanol, 1,2-propylene glycol, and glycerol on supported heteropoly acid (HPA) was studied using transient diffuse reflectance infrared fourier transform spectroscopy (DRIFTS). Tungstosilicic acid ($H_4[SiW_{12}O_{40}]$ denoted as $H_4SiW$), supported on neutral mesoporous alumina as a catalyst, was studied to investigate the formation of intermediate products and desired dehydration products on the catalyst surface. Both ethylene-containing species and surface-bound carboxyl species were detected for all three alcohols. The formation of ethylene was promoted at lower temperatures while an increased reaction temperature facilitated the formation of acetate products when ethanol was used. When 1,2-propylene glycol was used, surface-bound carboxyl species were found as major intermediate products; these might have formed from propanal produced from the hydration reaction catalyzed by acid sites on HPA. Intermediate species from more complicated reactions were detected on the catalyst surface when glycerol was used, including aldehyde, surface-bound carboxyl species, and alkene species. The results indicated that acid dehydration might be facilitated either by the addition of water or lowering the reaction temperature. The work provides insight into reaction pathways for bio-polyols, and therefore is informative for designing cost-effective and efficient chemical catalysis systems for the conversion of bio-renewables.

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## 1 Introduction

The main challenges for the current fossil-fuel-dependent energy structure are carbon dioxide emissions and resource shortages. There are several promising alternatives to fossil resources; bio-polyols—including bio-ethanol from biomass fermentation, glycerol from bio-diesel production, and other compounds from renewable resources containing multiple hydroxyl groups such as carbohydrates from biomass hydrolysis—are among those alternatives. These bio-renewables have the potential to provide for the production of both clean fuel and value-added chemicals, with the added advantage of nearly neutral $CO_2$ emissions [1, 2]. One of the unique characteristics of these bio-renewables is the existence of multiple hydroxyl groups in their molecular structures, as distinct from the structures of chemical compounds in petroleum or coal. These multiple hydroxyl groups present a unique conversion pathway to the production of fuel and value-added chemicals; however, the catalytic chemistry behind the pathway is not yet fully understood. Furthermore, compared to compounds with a single hydroxyl group, the reaction pathways for polyols are much more complicated due to the interaction among the multiple hydroxyl groups. Many problems are associated with the multiple hydroxyl groups, such as hydrogen bonding that causes low volatility of the polyols and high oxygen content that causes low heating values. Only a few studies [3, 4] have reported the information about unimolecular decomposition of protonated diols by the use of molecular model calculations, in which pinacol rearrangement and substitution

processes involve the formation of aldehyde and cyclized products after the loss of one or two water molecules.

Dehydration can effectively deoxygenate polyols by eliminating the hydroxyl groups and usually is the initial reaction step in the production of fuel components such as alkanes [5]. The dehydration reaction can be catalyzed by various solid acid catalysts, such as heteropoly acid (HPA) [6–12]. Because of the advantages of supported heterogeneous systems compared to unsupported ones, the behavior and stability of Keggin-type HPAs on several supports have been investigated [7, 8]. Alumina was selected as the support of HPA in this study, and investigations of HPA on other supports, such as silica, zeolite, and activated carbon are also in progress. For alumina-supported HPA catalysts, the formation of aluminum salt rather than the decomposition of the Keggin-type structure has been suggested for 12-molybdophosphoric acid and 12-tungstosilicic acid [9–12]. Interestingly, it seems that $H_4SiW$ supported on alumina is an efficient catalyst for the conversion of methanol to hydrocarbons [12]. Hanan et al. [13] also recently reported that in the catalytic dehydration of glycerol using several different HPAs supported on alumina and silica, alumina was, surprisingly, found to be superior to silica as a support material with regard to catalytic activity and acrolein selectivity, and tungsten-based HPAs showed outstanding performance and stability.

Transient diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) was used to acquire spectroscopic information of the intermediate species formed on the catalyst surface during the adsorption and dehydration of ethanol, 1,2-propylene glycol, and glycerol, which contains 1, 2, and 3 hydroxyl groups, respectively. This comparative information is important but is not available in the published literature, especially for 1,2-propylene glycol and glycerol. The different reactions of the intermediate species were examined using DRIFTS; the differences and associations among those intermediate species are discussed in order to shed light on the behavior of multiple hydroxyl groups during the dehydration of bio-polyols on the solid acid catalyst. Another aim of this study is to provide fundamental information about the influence of reaction conditions, such as the presence of water and the reaction temperature, on the formation of intermediate species. This study will contribute to a better understanding of bio-polyol dehydration, which will ultimately lead to cost-effective and efficient chemical catalysis systems for the conversion of bio-renewables to bio-fuels and bio-chemicals.

## 2 Experimental

### 2.1 Catalyst Preparation

A mesoporous neutral $Al_2O_3$ support (Alfa Aesar, USA), with a BET surface of 219 $m^2\ g^{-1}$ and an average pore size of 6.7 nm, was used in this study. Catalysts were prepared by impregnation of HPA onto the $A1_2O_3$ support, which had been previously annealed at 773 K. Tungstosilicic acid (Aldrich), $H_4[SiW_{12}O_{40}]$ (denoted as $H_4SiW$) was loaded onto the $Al_2O_3$ surface in an aqueous solution of $H_4SiW$ at room temperature for 12 h. Finally, the precipitate was calcined at 673 K for 1 h in a muffle furnace. The loading of $H_4SiW$ was controlled by varying the concentration of the $H_4SiW$ solutions for impregnation. An excessive 26.4 wt% $H_4SiW$ loading, higher than the level of irreversibly absorbed $H_4SiW$ [12], was used to ensure enough active phase on the support.

### 2.2 DRIFTS

DRIFTS spectra were recorded using a Varian 3100 FTIR spectrometer equipped with a high-sensitivity linearized mercury cadmium telluride (MCT) detector (Varian, USA). A cell (PIKE Technologies, USA) capable of high-pressure and high-temperature operation and fitted with ZnSe windows served as the reaction chamber for in situ adsorption and for the reaction measurements. Spectra were acquired at a resolution of 8 $cm^{-1}$ with the average of 256 co-additions. The amount of catalyst was 50 ± 0.5 mg. Catalyst samples were first purged with 100 mL $min^{-1}$ helium (He) flow at 30 K $min^{-1}$ until 673 K for 1 h, and then a background spectrum was obtained for the catalyst surface. For the injection of the reaction feedstock, a helium gas flow was passed through the feed solution container to carry the reaction material into the DRIFTS cell. For the investigation of the effects of the addition of water, 70 wt% glycerol solution was used to bring moisture and glycerol vapor into the reaction cell. To prevent the low-volatility sample from being condensed on the cell wall and ZnSe windows, the cell wall and window temperature were controlled to a temperature higher than that of sample evaporation in a helium atmosphere.

## 3 Results and Discussion

### 3.1 DRIFTS Analysis of Ethanol Adsorption and Dehydration

Figure 1a–c shows the spectra of adsorbed pure ethanol on the $H_4SiW/Al_2O_3$ catalyst at 250, 300 and 350 °C and different sample adsorption times. Ideally, ethylene will be produced from the dehydration of ethanol. The bands at 3080 and 3010 $cm^{-1}$ are, respectively attributed to the asymmetric and symmetric stretch modes of carbon-to-hydrogen bond in the ethylene functional groups [14]. The band observed at 1665 $cm^{-1}$ represents the stretch of the carbon-to-carbon double bond in the ethylene functional

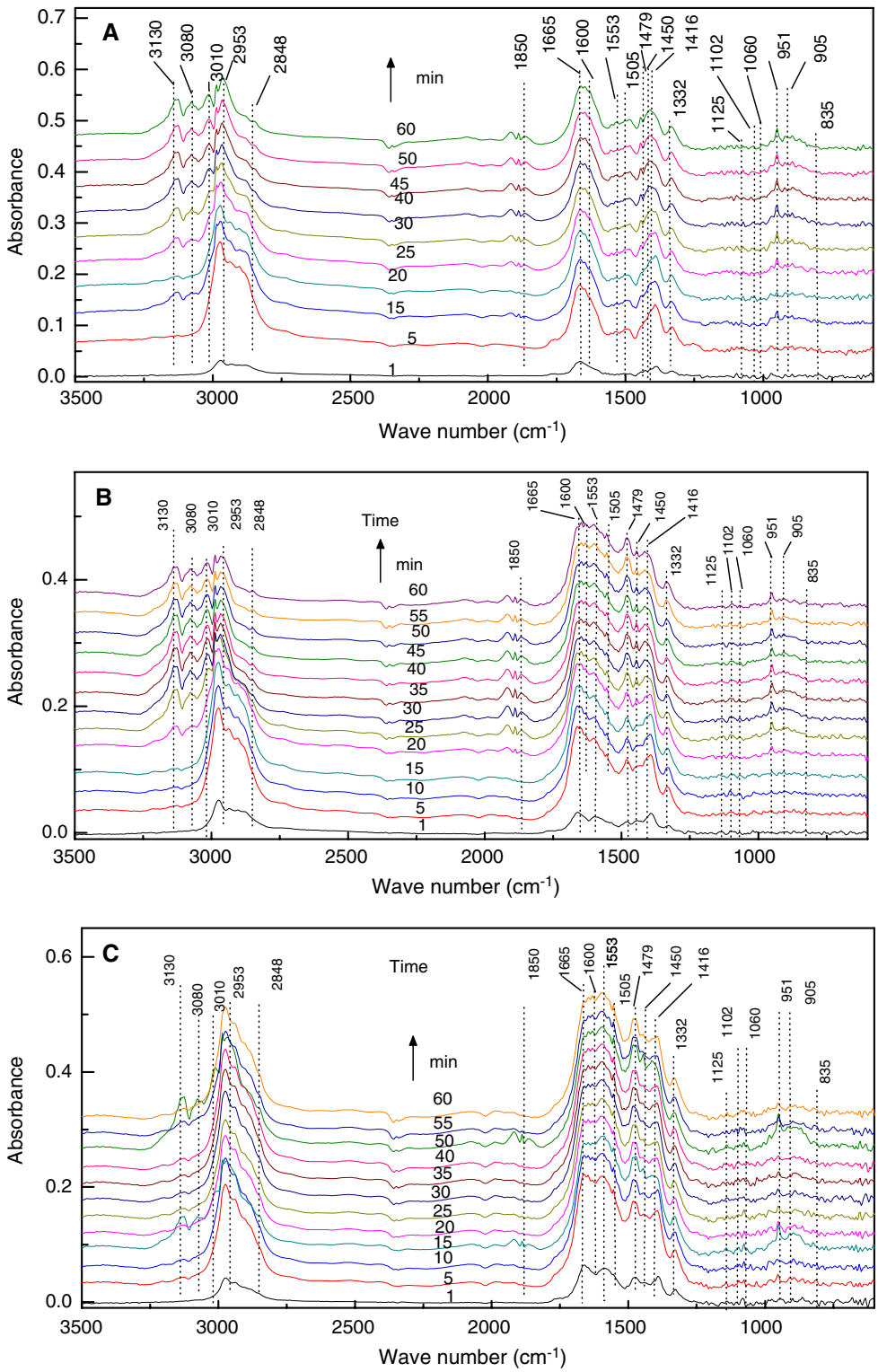


**Fig. 1** Reaction of pure ethanol on $H_4SiW/Al_2O_3$ at 250 °C (**a**), 300 °C (**b**) and 350 °C (**c**) and different adsorption times

group [14]. The weak bands observed at 905 $cm^{-1}$ (terminal alkene) and 951 $cm^{-1}$ are related to the twist and bend modes of the ethylene structure, respectively, and the band at 1850 $cm^{-1}$ can be attributed to the overtone frequency of the out-of-plane bend of ethylene structure [14]. These bands are indicators of the ethylene formation on the catalyst surface because of the dehydration of ethanol, probably catalyzed by acid sites on HPA and support. It has been reported the adsorption of ethylene at similar temperatures as those in this study, such as ethylene epoxidation over $Ag/Al_2O_3$ at around 200–210 °C [15], and adsorption of ethylene on Ir (111) surface at 230 °C

[16], showing that the adsorptive species on Ir (111) can be well detected by high resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy. Interestingly, the researchers also found that at $T > 180$ °C (450 K) the saturated coverage after $C_2H_4$ exposure was higher than that at 27 °C (300 K); the proposed mechanism was the formations of new polymer species from ethylene on the catalyst surface at high temperatures (>180 °C), which were absent in $C_2H_4$ adsorption at ambient temperature (27 °C) [16]. This previous result indicated that oligomers of ethylene and aromatic structures can be formed before ethylene desorption from the catalyst surface under relatively high temperatures. In our observation (Fig. 1), these typical bands of ethylene functional groups increase with the increase of reaction time within the first 30 min of reaction; this may be a result of the lower concentration of the formed ethylene species, which take some time to reach adsorption/desorption equilibrium on the catalyst surface.

Ethanol molecules can also be dissociatively adsorbed on the $Al_2O_3$ sites, forming ethoxide species. The bands at 1060, 1102, 1416, 1479, 2848, and 2953 $cm^{-1}$ correspond to different vibration modes of ethoxy species, which were formed by dissociative adsorption of ethanol onto $Al_2O_3$ in bidentate and mono-dentate modes [17–19]. In addition to the bands of ethoxy species, there are also weak bands at 1332 and 1553 $cm^{-1}$, which are assigned to the $\nu$(OCO) symmetric and asymmetric vibrational modes of acetate species, respectively [19–22], indicating that ethoxy species have been oxidized to acetate species, due to the redox properties of the support and HPA. This reaction might involve the dehydrogenation of ethoxy species to acetaldehyde (1700 $cm^{-1}$), which may be further dehydrogenated to acetyl species (1640 $cm^{-1}$) and which then reacts with oxygen from the support to produce the acetate species (1553, 1332 $cm^{-1}$) [17, 18].

For the observation of temperature effect, it is noteworthy to point out that the bands of acetate species corresponding to 1553 and 1332 $cm^{-1}$ are significantly higher at 300 and 350 °C, comparing with those at 250 °C. Intensity of the characteristic ethylene bands shows no significant change at 300 °C and tends to be unstable at 350 °C. This phenomenon might result from the higher desorption rate or the formation of other polymeric products from ethylene at higher temperatures. Increasing reaction temperature will facilitate the formation of acetate and surface-bound carbonate products and finally the formation of decomposition products such as $CH_3CHO$, $CH_4$, CO, $CO_2$, etc. [17, 19, 20]. The more significant intensity changes of the acetate characteristic bands that result from temperature increases, compared with the effect of reaction time, indicate that temperature plays a more important role than reaction time during the dehydration reaction.

Bands at 3130 $cm^{-1}$ (corresponding to C($sp^2$)–H stretch vibration), 1600, 1505, and 1450 $cm^{-1}$, correspond to aromatic stretch vibration modes; bands of 1600 and 1505 $cm^{-1}$ are in symmetric modes and 1450 $cm^{-1}$ is in a sideways mode; together with the weak band detected at 835 $cm^{-1}$ (C–H in plane deformation), these bands indicate the formation of oligomer ethylene structure or aromatic structure on the catalyst surface, providing strong evidence of the presence of intermediate products for coke formation from the reaction of ethanol on acid catalyst surface. It has been proposed that benzene formation on Pt/$CeO_2$ metal catalyst takes place via the reaction of surface-bound crotonaldehyde and acetaldehyde species [19, 20]. However, our results suggest that ethylene oligomer and aromatic structures might be the major source of formation of intermediates to coke in the presence of acid catalysis and ethanol, supporting the proposed pathway for coke formation via ethylene [23]. The characteristic bands of ethylene oligomer and ethylene appear simultaneously, suggesting that the oligomer structure formation reaction is faster than that of the ethylene formation reaction.

### 3.2 Reaction of Propylene Glycol on the $H_4SiW/Al_2O_3$

Figure 2 shows the spectra obtained by adsorption of pure 1,2-propylene glycol on $H_4SiW/Al_2O_3$ at 300 °C and different adsorption times. The bands at 2975, 2910, 2900, 2870, 1070, and 1115 $cm^{-1}$ are due to physically adsorbed propylene glycol and dissociative adsorption products. The weak bands at 3080 and 1650 $cm^{-1}$ can also be observed, indicating the formation of ethylene-containing species. The weak band at 1736 $cm^{-1}$ can be assigned to (C=O) of adsorbed propanal, which may be formed in this reaction. There are significant bands at 1326 and 1579 $cm^{-1}$, which are assigned to the $\nu$(OCO) symmetric and asymmetric vibrational modes from propanoic acid or propanone that were formed on the catalyst surface.

Two possible mechanisms for the dehydration reaction of propylene glycol have been proposed, utilizing a density functional theory (DFT) calculation to account for the rearrangement of propylene glycol to propanal [3]. The first is the rearrangement with a hydride shift occurring in concert with the loss of a water molecule. The second is an acid catalyzed dehydration reaction proceeding through the enol to yield propanal. Chompoonut et al. [4] using the DFT, also calculated the acid-catalyzed models on reaction mechanisms of pinacol rearrangement of propylene glycol to propanal and propanone at 298.15 K. In our work, the weak ethylene-characteristic bands and the aldehyde-characteristic bands detected on the catalyst surface suggested that propanal formed by the dehydration catalyzed by the acid sites was the major pathway, rather than propanone.

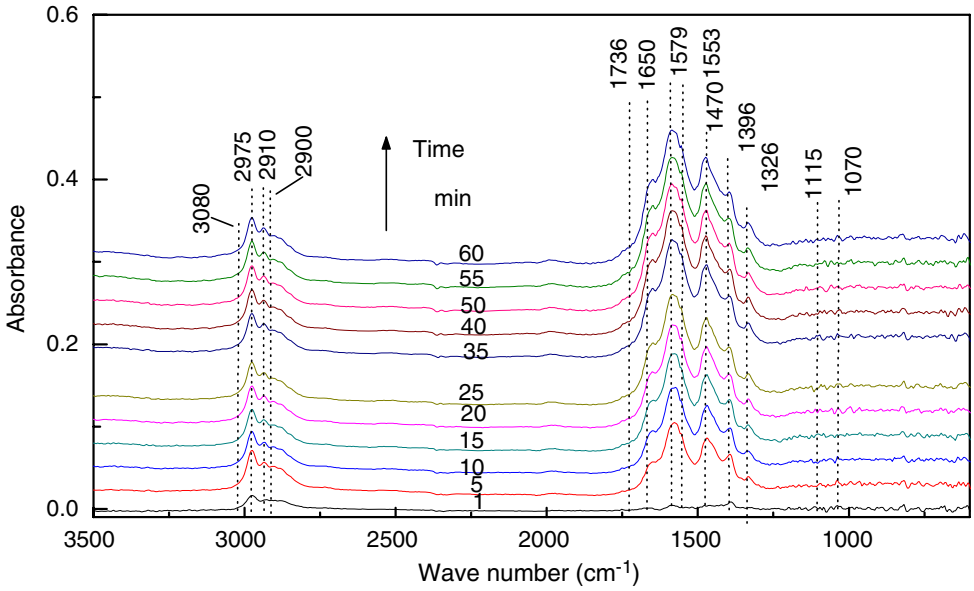


**Fig. 2** Reaction of pure propylene glycol on $H_4SiW/Al_2O_3$ at 300 °C and different adsorption times

### 3.3 Reaction of Glycerol on $H_4SiW/Al_2O_3$

Pure glycerol adsorption experiments were conducted on the $H_4SiW/Al_2O_3$ at 300 °C. Multiple dehydration products, including acrolein, which is an important value-added chemical for the polymer industry, might be produced. Figure 3 shows the DRIFTS spectra of adsorbed glycerol on the $H_4SiW$ catalyst at different sample adsorption times. The bands at 1050, 1120 $cm^{-1}$ correspond to the C–O, which might be in bidentate and mono-dentate modes and which was formed by the dissociative adsorption of the glycerol. In addition to the bands of adsorption species, bands at 1589 and 1390 $cm^{-1}$ were also detected; these are assigned to the $\nu$(OCO) symmetric and asymmetric vibrational modes, respectively, as mentioned above. The appearance of these bands indicates that adsorptive state of glycerol could also be oxidized to surface-bound carboxyl species, either by the redox properties of the support or the HPA. Moreover, a well-defined band at 1723 $cm^{-1}$ became progressively visible. This band can be also assigned to physical adsorption of aldehyde species. These intermediates may react with oxygen from the support to produce surface-bound carboxyl species (1589, 1390 $cm^{-1}$) [14, 19, 20]. Characteristic bands of ethylene-containing species at

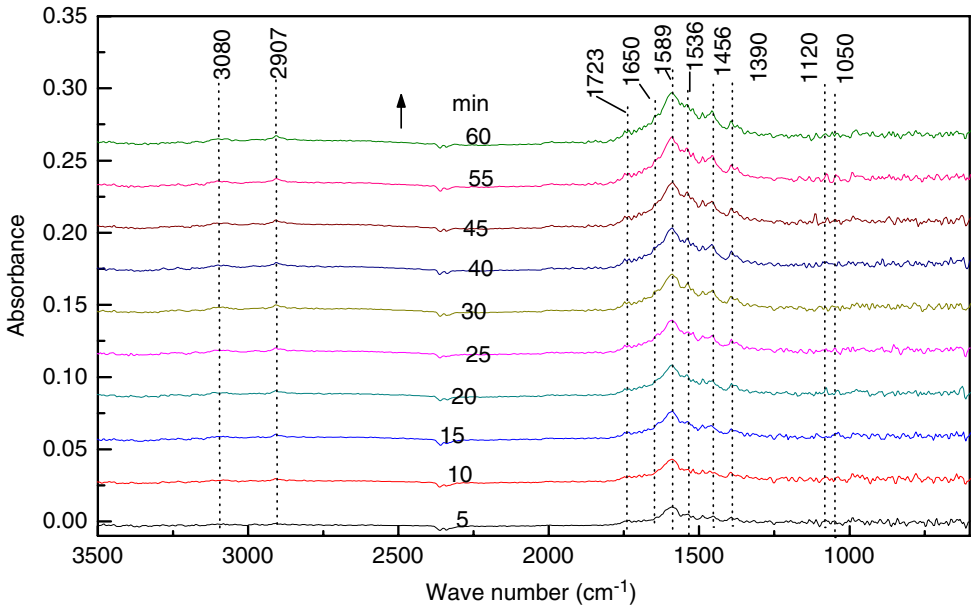


**Fig. 3** Reaction of pure glycerol on $H_4SiW/Al_2O_3$ at 300 °C and different adsorption times

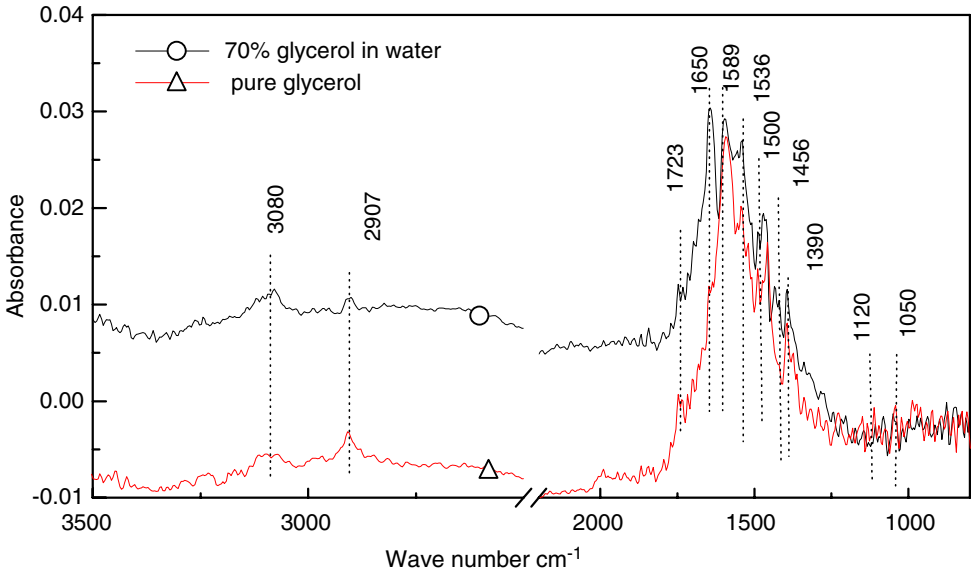


**Fig. 4** Effect of water on the dehydration of glycerol on $H_4SiW–Al_2O_3$ (70% glycerol solution, 300 °C, 100 mL $min^{-1}$ helium)

3080, 1650 $cm^{-1}$ (C=CH) were also observed, indicating that multiple reaction pathways, such as acid catalysis and a redox mechanism, occurred on the catalyst surface, both of which might be catalyzed by the HPA catalyst. Calculating the dehydration of neutral glycerol using molecular modeling with DFT, Mark et al. [24] indicated that the high activation energy of glycerol without catalyst is 70.9 kcal $mol^{-1}$, and it decreases to lower than 25 kcal $mol^{-1}$ in the presence of an acid catalyst. This result suggests that dehydration of glycerol without a catalyst can only occur at relatively high temperatures such as those in pyrolysis or combustion reactions. The addition of an acid catalyst will allow substantially lower dehydration temperatures involving triols [24].

Crude glycerol as a byproduct of biodiesel production always contains some water, typically within the range of 5–40 wt%. To understand the effect of water on the reaction pathway, aqueous glycerol solution at 70 wt% of glycerol was used as feedstock. Figure 4 compares the spectra of pure glycerol and glycerol solution. The band at 1650 $cm^{-1}$ (corresponds to C=C stretch mode) is significantly higher than that without water addition in the system. Chompoonut et al. [4] pointed out the effect of water interacting with the transition states of three concerted pathways and thus decreasing the product ratio of propanal to propanone when propylene glycol is used as a reactant in the DFT calculation. Our result showed that adsorptive species were significantly changed in the presence of water using glycerol as feedstock, indicating that reaction mechanism is changed in the presence of water vapor under this condition. Hanan et al. [13] obtained higher glycerol conversion and acrolein selectivity (98.4 and 63.6 mol%, respectively under the condition of 275 °C using 10 wt% of glycerol solution) on alumina-supported $H_4SiW$ than on other silica supports. It was also revealed that both Lewis acid and Brønsted acid centers are present in this catalysis system [13], in agreement with our IR experimental result of pyridine adsorption. One possible reason for the mechanism change is that the presence of water vapor in this catalysis system can hydrate a portion of the Lewis acid centers on catalyst surface forming Brønsted acidity centers under this reaction condition [13].

Figure 5 shows the effect of temperature on spectra of the dehydration on $H_4SiW/Al_2O_3$ performed by purging helium through a 70% glycerol solution. Similar bands were obtained, indicating that the reaction pathway does not change much with the change of temperature from 275 to 300 °C. Those bands at 1050 and 1120 $cm^{-1}$, which can be attributed to the C–O bands of dissociative adsorptive glycerol, are higher at lower temperature (275 °C). The result indicated that more glycerol can be adsorbed on the catalyst under a lower temperature because of the low volatility of glycerol (the boiling point is 290 °C). The relative ratio of the band at 1650 $cm^{-1}$ to the band at 1589 $cm^{-1}$ significantly increases with the decrease of temperature from 300 to 275 °C, indicating that ethylene bond formation is favored at a lower temperature. In a kinetic study of glycerol dehydration, Hanan et al. [13] found that the selectivity to acrolein decreased from 63.6 to 58.9% while the yield of unrecovered products increased from 14.7 to 16.5% with the reaction temperature increase from 275 to 300 °C using a similar $H_4SiW/Al_2O_3$ catalyst, accordant to our DRIFTS experimental results. This result suggests that the acid catalysis effect of $H_4SiW$ is more significant at a lower temperature because the higher ethylene bonds are generated from the dehydration pathway of glycerol at lower temperatures.

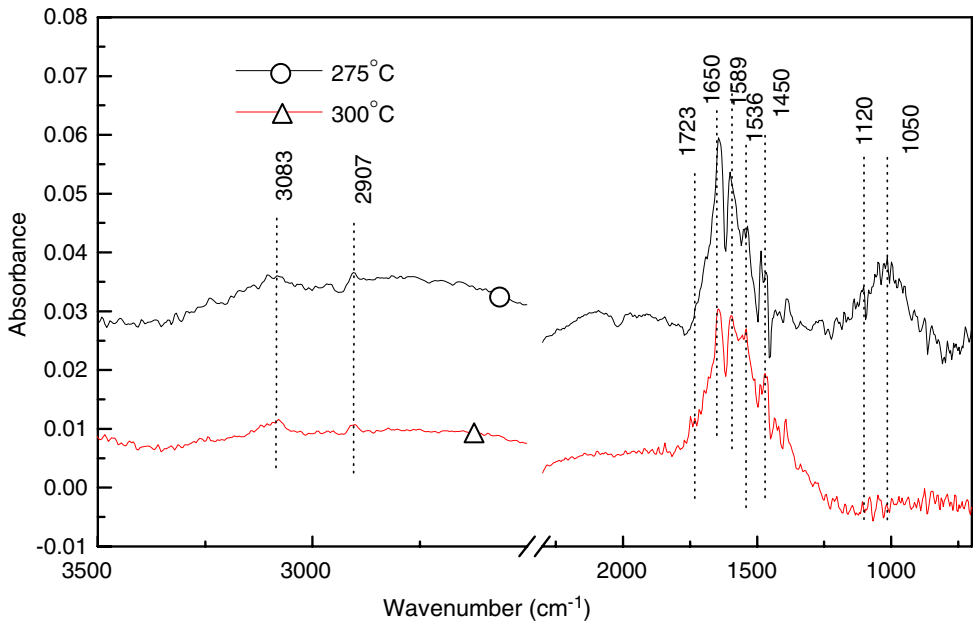


**Fig. 5** Effect of temperature on the dehydration of glycerol on $H_4SiW$–$Al_2O_3$. 70% glycerol solution, 100 mL $min^{-1}$ helium)

## 4 Discussion

Based on the information provided by DRIFTS, reaction pathways for ethanol, 1,2-propylene glycol, and glycerol dehydration over $H_4SiW/Al_2O_3$-based catalysts are proposed in Fig. 6.

In Fig. 6a, the reactant ethanol molecules diffuse to the surface of the catalyst to form adsorptive states, either physical adsorption as ethanol molecules or dissociative adsorption on the support, forming ethoxide species. One pathway is catalyzed by the protons provided by $H_4SiW$. The ethoxide species can also be dehydrated to ethylene or the oxidized form, acetaldehyde, either by an additional hydrogen abstraction or by lattice oxygen oxidation on the surface. Acetaldehyde molecules may lead to the formation of acetate species. This surface species may desorb or further oxidize to give carbonate species, especially at higher temperatures, which can be then desorbed as $CO_2$ [19, 20]. The low reaction temperature of 250 °C favors the formation of ethylene. Increasing the temperature favors the formation of oxide species.

In Fig. 6b for propylene glycol, the major intermediate products are detected as such oxidized products as surface-bound carboxyl groups and propanal. The acid catalysis

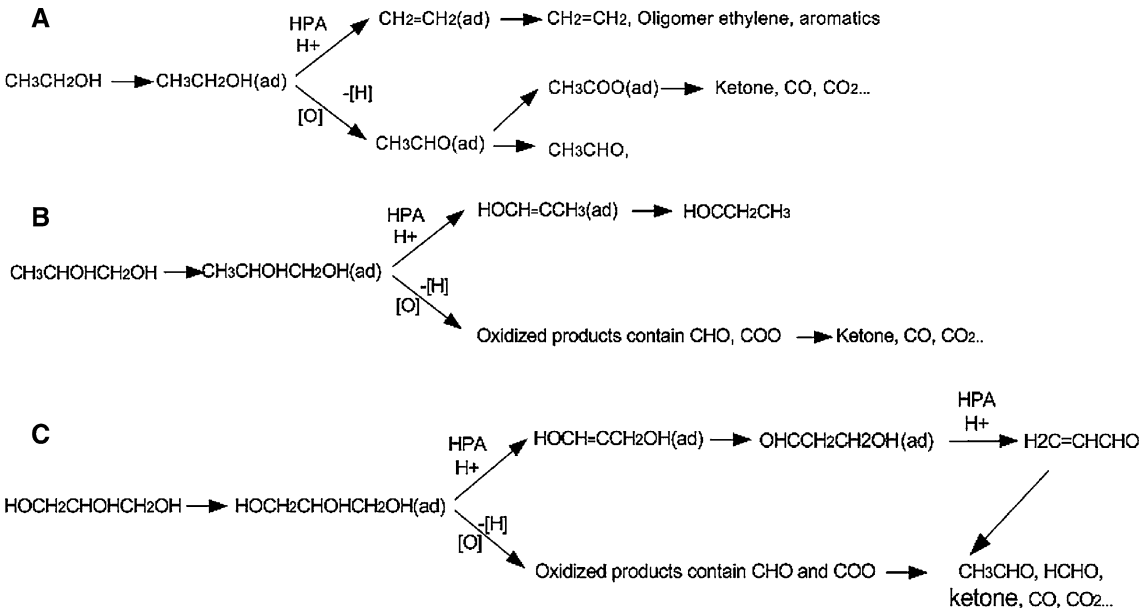


**Fig. 6** Proposed pathway schemes of multiple –OH reactants on $H_4SiW/Al_2O_3$ surface

mechanism will facilitate the formation of carbonium and then enol, which is instantaneously isomerized to a more stable structure, propanal. The propanal can also be formed by oxidized reaction via an additional hydrogen abstraction or lattice oxygen oxidation. Surface-bound carboxyl species can also be formed by further oxidation reaction. Both of the weak characteristic bands of ethylene and aldehyde were detected on the catalyst surface, suggesting that propanal formed by acid site catalysis was the major pathway.

The situation becomes more complicated with an additional –OH group presence when glycerol is used. As shown in Fig. 6c, glycerol, with three –OH groups, causes more complicated pathways on an $H_4SiW/Al_2O_3$ surface. The acid catalysis mechanism will facilitate the formation of carbonium ion and subsequently a dihydroypropene structure, which might lead to acrolein by a further dehydration reaction and/or keto-enol tautomerism to 3-hydroxypropenal. A reverse aldol mechanism which converts 3-hydroxypropanal to formaldehyde and acetaldehyde might also happen under these conditions [1]. Our result indicates that acrolein formation may be favored when water is added into the system. This result also indicates that anhydrous condition and a higher temperature favor the formation of oxidized products.

## 5 Conclusions

Selective catalytic dehydration of alcohols, propylene glycol, and glycerol on supported HPA catalyst was studied using the DRIFTS technology. Tungstosilicic acid supported on neutral alumina was studied to investigate the formation of intermediate products toward the production of desired dehydration product on the catalyst surface. Both ethylene and oxidized compounds can be formed on the catalyst surface for all these alcohols. The formation of ethylene is promoted at lower temperatures while increasing the temperature will facilitate the formation of acetates and carbonate products when ethanol is used as the feedstock. In the case of 1,2-propylene glycol as feedstock, surface-bound carboxyl species were found as the major intermediate products, which might be formed from propanal catalyzed by acid sites on HPA. More complicated reaction intermediate species were detected on the catalyst surface for glycerol, also including aldehyde, surface-bound carboxyl species, and acrolein; the results also indicate that anhydrous condition and a higher temperature favor the formation of oxidized products. The information gained from this study will be applied toward understanding the design of the polyols reaction system and value-added chemical products that can be produced from renewable bio-polyols.

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