Aqueous Phase Hydrodeoxygenation of Polyols over Pd/WO₃-ZrO₂: Role of Pd-WO₃ Interaction and Hydrodeoxygenation Pathway

Changjun Liu[§], Junming Sun[†], Heather M. Brown[‡], Oscar G. Marin-Flores[†], Tim Bays[‡], Ayman M. Karim^{*†‡} and Yong Wang^{*†,‡},

[§] Multi-phase Mass Transfer and Reaction Engineering Laboratory, College of Chemical Engineering, Sichuan University,

Chengdu 610065, China

[†] The Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman

Washington 99164, United States

[‡] Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, Washington 99352, United States

[†] Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

* Author to whom correspondence should be addressed.

wang42@wsu.edu (Y.Wang); amkarim@vt.edu (A.M. Karim)

Abstract:

Aqueous phase processing of biomass derived sugar alcohols is one of the promising routes to convert biomass into fuels and chemicals. Bifunctional catalysts are critical in the aqueous phase hydrodeoxygenation of sugar alcohol. Understanding the interaction between metal and acidic metal oxides as well as the hydrodeoxygenation pathways will help develop more efficient bifunctional catalysts. Here, tungstated zirconia supported palladium catalysts were prepared and further characterized using nitrogen sorption, X-ray diffraction, FT-IR analysis of adsorbed pyridine, CO chemisorption and diffuse reflectance UV-vis. Strong interaction between palladium and WO₃ in addition to a synergetic effect of the acidic and metallic sites were found to promote the aqueous phase hydrodeoxygenation of ethylene glycol. H-D exchanging experiments

confirmed that the aqueous phase hydrodeoxygenation follows a dehydration-hydrogenation pathway. The hydrogenation of the dehydration products shifts the dehydration-hydration equilibrium towards the dehydration pathway and leads to highly selective C-O cleavage.

Keywords: Aqueous phase hydrodeoxygenation; biomass; zirconia; bifunctional catalyst

1. INTRODUCTION

The depletion of fossil resources and increasing global warming issues have urged both the scientific and industrial communities to explore renewable resources such as biomass [1]. Biomass is considered the only renewable carbon resource for our industrial society [2]. Lignocellulosic biomass, which is composed of 65-82 wt.% cellulose and hemicelluloses[3], has been extensively studied in an effort to produce liquid fuels and valuable chemicals. Catalytic fast pyrolysis can directly convert lignocellulosic biomass into hydrocarbons but with low carbon yields [4]. On the other hand, well-developed hydrolysis processes are capable of deconstructing cellulose and hemicelluloses in lignocellulosic biomass into their corresponding sugars (e.g., glucose, fructose, xylose) and separating them from the insoluble lignin [5-7]. Biomass derivatives have high oxygen content, low volatility, and high solubility in water. Their low thermal stability and highly reactive nature are more suitable to catalytic aqueous phase processing at moderate temperatures [2]. With aqueous phase processing, cellulose and hemicellulose derived intermediates can be more selectively converted into desired fuel products via a tandem reaction pathway [8].

Selective removal of oxygen from these biomass-derived intermediates without excessively breaking C-C linkages is one of the key challenges in fuel production [9]. Hydrodeoxygenation (HDO) is the common step in all processes that currently exist for the thermochemical conversion

of biomass to liquid fuels/chemicals (e.g. liquefaction fast pyrolysis, catalytic fast pyrolysis, and aqueous phase conversion of carbohydrates). Controlled aqueous phase HDO of the hydrolysis products (monoses/polyols) from cellulose and hemicellulose is the primary step to achieve high selectivity in these processes [8]. Bifunctional catalysts with appropriate metallic and acidic sites were found to be capable of catalyzing the aqueous phase HDO of polyols [10, 11]. The selectivity to hydrocarbon products can be improved by catalysts with more hydrogenating metallic phases on supports with stronger acidity [12]. A wide range of Pt promoted solid acid catalysts has been tested [13]. However, further understanding of the HDO reaction mechanism and optimizing of the catalysts are necessary for improving the selectivity to mono-oxygenates.

WO_3 is used as a solid acid in many acid catalyzed processes [14-17] including dehydration reactions by tungstated zirconia [18, 19]. Palladium is a cheaper hydrogenation noble metal than platinum. The combination of Pd and tungstated zirconia ($\text{Pd}/\text{WO}_3\text{-ZrO}_2$) has been studied by Dedsuksophon et al. for hydrolysis/dehydration/aldol condensation/hydrogenation of lignocellulose and carbonhydrates [20, 21]. In this work, Pd/ZrO_2 catalysts promoted by WO_3 were studied in the aqueous phase HDO of polyols with the focus on the selectivity to C-O cleavage and C-C cleavage. Ethylene glycol was used as the surrogate for polyols to simplify the reaction routes and products. The interaction between palladium and WO_3 as well as the aqueous phase HDO mechanism of polyols were elucidated.

2. EXPERIMENTAL

2.1 Preparation of Catalysts.

Zirconia (ZrO_2) and tungstated zirconia ($\text{WO}_3\text{-ZrO}_2$) purchased from Saint-Gobain Nor-Pro

were used as the starting material. The nominal tungsten loading of tungstated zirconia is 12.5 wt.%. Both zirconia and tungstated zirconia supported palladium catalysts were prepared by incipient wetness impregnation. Palladium(II) nitrate hydrate $\text{Pd}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ purchased from Sigma-Aldrich was used as the precursor of palladium. A given amount of palladium nitrate hydrate was dissolved into the 2 M NH_4NO_3 solution to achieve better Pd dispersion. After impregnation the resultant catalysts were dried at 120 °C for 4 h then calcined in static air at 400 °C for 6 h with a ramping rate of 2 °C·min⁻¹. The nominal palladium loading is 2.0 wt.% and the catalyst was labelled as 2Pd/WO₃-ZrO₂. Pd/WO₃-ZrO₂ catalysts of smaller Pd particle sizes were prepared to investigate the effect of Pd particle size on the activity and selectivity by following the same procedure with Pd loadings of 0.5 wt.% and 1.0 wt.%. Pd/WO₃-ZrO₂ catalysts with Pd loadings of 0.1 wt.% and 0.25 wt.% were prepared and tested in UV-vis-DRS to minimize the effect of the black color of the reduced catalysts on the pre-edge energy analysis of WO₃.

2.2 Catalyst Characterization

Crystalline structures of the catalysts were characterized by X-ray diffraction (XRD) on a Philips X'pert diffractometer with a copper anode ($K\alpha_1=0.15405$ nm) operating at 40 kV and 50 mA. Nitrogen adsorption-desorption isotherms were performed at -196 °C with an automatic adsorption meter (Quantachrome instruments autosorb-6). The samples were pretreated at 150 °C for 6 h under vacuum. The surface areas were calculated from adsorption values at five relative pressures (P/P_0) ranging from 0.10 to 0.31 using the Brunauer-Emmett-Teller (BET) method. The pore volumes were determined from the total amount of N₂ adsorbed between $P/P_0=0.05$ and $P/P_0=0.98$. Infrared spectra of adsorbed pyridine (IR-Py) were collected on a Bruker Tenser 27

FTIR spectrometer. Reflectance spectra of the catalysts were recorded with a Varian Cary 5000 UV-Vis-NIR spectrophotometer in the wavelength range from 200 to 800 nm at a resolution of 0.333 nm. The pulse CO chemisorption experiments were performed on a Micromeritics Autochem II 2920 Chemisorption Analyzer with a TCD detector at 40 °C using 10% CO in helium. The temperature-programmed desorption of ethanol and isopropylamine were carried out on a home-made TPD system with a bubbler to introduce the vapors. The samples were first reduced at 300 °C for 1 h by H₂, the adsorption step was performed at room temperature for 1 h then purged with helium for another hour. Thereafter, the desorption profile was recorded by a Pfeiffer OmniStar Quadrupole Mass Spectrometer under helium with a ramping rate of 10 K·min⁻¹.

2.3 Catalytic Reaction

The catalytic activity tests were carried out in a fixed bed reactor with both ethylene glycol solution and hydrogen fed from the top of the reactor. A given amount of catalyst with the particle size about 100 µm was loaded in the middle of the reactor. Dense zirconia ceramic of similar particle size was packed below and above the catalyst section so that the feed could be evenly distributed across the reactor section and preheated to the reaction temperature before it reached the catalyst zone. The catalyst was reduced *in situ* at 300 °C in 40 sccm H₂ for 1 h and then cooled down to reaction temperature before starting the reaction. Ethylene glycol was diluted to 10 wt.% in water and used as liquid feedstock. The reaction temperature was set to 240 °C and the system was pressurized to 7.34 MPa (1050 psig) by high purity H₂. The product stream from the reactor was chilled to 4 °C. The liquid products were collected and analyzed using a Waters high performance liquid chromatograph (HPLC) with a refractive index detector while the gases were analyzed online by an Agilent micro 3000 chromatograph with a thermal conductivity detector

(TCD). The discharged gas flow rate was recorded with a mass flow meter. The H-D exchange experiments were performed under the same reaction conditions. The system was completely purged with D₂O and H₂ before experiments using 10 wt.% ODCH₂CH₂OD in D₂O as the liquid feed, and was purged thoroughly with H₂O and H₂ when using 10 wt.% CD₃OH in H₂O feed. The resultant liquid reaction mixtures were analyzed by ¹H NMR.

3. RESULTS

3.1 Characterization

Table 1 Physicochemical properties of the supports and catalysts

Sample	Pd	W	Surface	Pore	Pulse	Pd particle
	loading	loading	area	volume	chemisorption.	size ^a
	wt.%	wt.%	m ² ·g ⁻¹	cm ³ ·g ⁻¹	CO/Pd	nm
ZrO ₂	-	-	99	0.30	-	-
2Pd/ZrO ₂	2.0	-	101	0.31	0.86	1.30
WO ₃ -ZrO ₂	-	12.5	116±2	0.23	-	-
2Pd/WO ₃ -ZrO ₂	2.0	12.5	110±2	0.22	0.17	6.73
1.0Pd/WO ₃ -ZrO ₂	1.0	12.5	-	-	0.45	2.46
0.5Pd/WO ₃ -ZrO ₂	0.50	12.5	-	-	0.70	1.60

^a palladium particle sizes were estimated by $D=6(v_m/a_m)/d_{VA}$ [22], where D is the metal dispersion, d_{VA} is the mean particle size in angstrom, $v_m = 14.70 \text{ \AA}^3$ is the volume occupied by a Pd atom in bulk metal, $a_m = 7.93 \text{ \AA}^2$ is the area occupied by a surface Pd atom.

Figure 1 XRD spectra of a) $\text{WO}_3\text{-ZrO}_2$ and b) $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$

Table 1 shows that tungstated zirconia has slight higher BET surface area than zirconia. The impregnation of palladium onto zirconia does not significantly change the BET surface area possibly due to good dispersion of Pd on the surface as indicated by the CO chemisorption. The impregnation of palladium onto the tungstated zirconia only leads to the slight decrease of BET surface area from $116 \text{ m}^2\cdot\text{g}^{-1}$ to $110 \text{ m}^2\cdot\text{g}^{-1}$. The XRD spectra (Figure 1) shows that tetragonal tungstated zirconia is a major phase and a peak at 40.3° corresponding to palladium particles of an average diameter about 6.73 nm was observed.

Figure 2 IR-Py spectra of a) ZrO_2 , b) $\text{WO}_3\text{-ZrO}_2$, c) $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$

Reduced at 300°C for 1 h, spectra collected at 150°C

Pyridine FT-IR was employed to characterize the acidic nature of the supports and catalyst (Figure 2). Pyridine adsorption was performed at 150 °C and then the spectra were collected at the same temperature after purging with helium for 30 minutes. The band at 1543 cm^{-1} is known to be due to $\text{N}^+\text{-H}$ stretching of pyridinium ions and is used to characterize the protonic acid sites along with auxiliary peaks at 1489 cm^{-1} , 1620 cm^{-1} and 1640 cm^{-1} [23-25]. $\text{WO}_3\text{-ZrO}_2$ and $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$ present both Brønsted acidity and Lewis acidity while zirconia itself shows only Lewis acidity. The presence of WO_3 in ZrO_2 introduces Brønsted acidic sites to the catalysts.

Figure 3 Diffuse Reflectance UV-vis absorption spectra of $\text{WO}_3\text{-ZrO}_2$ a) without palladium, b) Pd particle size of 1.48 nm, c) Pd particle size of 2.03 nm.

$\text{Pd}/\text{WO}_3\text{-ZrO}_2$ catalysts of Pd loadings higher than 0.5 wt.% were black after reduction and showed strong absorption of visible light. It is impossible to characterize the WO_3 domain size using their pre-edge adsorption energy. To understand the effect of Pd on WO_3 aggregation, $\text{Pd}/\text{WO}_3\text{-ZrO}_2$ catalysts were prepared by lowering the Pd loading to 0.1 wt.% and 0.25 wt.% with Pd particle sizes estimated by CO-chemisorption of 1.48 nm and 2.03 nm respectively. The WO_3 domain sizes were determined by the absorption edge energy with the diffuse reflectance UV-vis spectra (Figure 3). It is known that absorption edge energy decreases with increasing WO_3 domain

size [16]. Figure 3 shows the WO_3 domain sizes of the catalysts are somewhere between the bulk monoclinic WO_3 (2.59 eV) of six neighboring octahedra and the W_{12} cluster in ammonium metatungstate (3.23 eV) [16]. The impregnation of palladium onto $\text{WO}_3\text{-ZrO}_2$ resulted in the increase of WO_3 domain size as suggested by increased absorption edge energy (Figure 3). It is likely that the larger palladium particle size of 0.25Pd/ $\text{WO}_3\text{-ZrO}_2$ leads to larger WO_3 domain size as indicated by the lower absorption edge energy (Figure 3). However the detailed mechanism of WO_3 domain size growth is not clear yet.

3.2 Catalytic activity

Figure 4 Products distribution with/without WO_3

Feed: 10 wt.% ethylene glycol, $T=240\text{ }^{\circ}\text{C}$, $P=1050\text{ psig}$, $\text{H}_2/\text{C}=2$, $\text{WHSV}=1.10\text{ g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for

2Pd/ZrO₂ and $0.23\text{ g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for 2Pd/ $\text{WO}_3\text{-ZrO}_2$

Figure 5 Products distribution over Pd/WO₃-ZrO₂ catalysts of different Pd particle size

Catalysts: Pd/WO₃-ZrO₂ with 0.5 wt.%, 1 wt.% and 2 wt.% Pd loadings corresponding to 1.60,

2.46 and 6.73 nm Pd particle sizes, respectively; Carbon balance: 100±2%; Feed: 10 wt.%

ethylene glycol. T=240 °C, P=1050 psig, WHSV= 0.25-0.7 g·g⁻¹·h⁻¹;

2Pd/ZrO₂ and 2Pd/WO₃-ZrO₂, having the same palladium loading (Table 1), were tested in aqueous phase HDO of ethylene glycol and Figure 4 compares the product at a similar conversion of ~14%. Carbon oxides, methanol, methane, ethanol, acetaldehyde, acetic acid and ethane were the main products of aqueous phase HDO of ethylene glycol. Carbon oxides, methanol and methane are a result of C-C bond cleavage. Although the CO-chemisorption indicates that 2Pd/WO₃-ZrO₂ has a larger Pd particle size than 2Pd/ZrO₂ (Table 1), 2Pd/ZrO₂ shows much higher selectivity to CO and CO₂ than 2Pd/WO₃-ZrO₂. The presence of WO₃ largely improves the selectivity to ethanol. This suggests that the reaction pathways on the two catalysts are different. The effect of palladium particle size on activity and selectivity of Pd/WO₃-ZrO₂ catalysts was investigated by preparing catalysts with 0.5 wt.%, 1 wt.% and 2 wt.% Pd loadings corresponding to estimated Pd particle sizes of 1.60, 2.46 and 6.73 nm (Table 1), respectively. Figure 5 shows that the products distribution is not significantly affected by the palladium particle size.

4. DISCUSSION

4.1 Effect of WO₃ on Pd/ZrO₂ in aqueous phase HDO of ethylene glycol

Removal of oxygen without unnecessarily breaking the C-C bond is preferable in aqueous phase HDO of polyols since the resultant higher carbon-chain alcohols are better feeds for the subsequent transformation process over zeolites [26]. Here a C-O to C-C bond cleavage ratio was defined by equation (0) to differentiate the selectivity between C-O and C-C bond cleavage of catalysts.

$$\frac{C-O}{C-C} = \frac{\text{ethanol} + \text{acetaldehyde} + \text{ethane} \times 2 + \text{acetic acid}}{\sum C_1 \text{ products} / 2} \quad (0)$$

Figure 6 Comparison of the selectivity to C-O and C-C bond cleavage

Feed: 10 wt.% Ethylene glycol, T=240 °C, P=1050 psig, H₂/C=2, WHSV=1.10 g·g⁻¹·h⁻¹ for

2Pd/ZrO₂ and 0.23 g·g⁻¹·h⁻¹ for 2Pd/WO₃-ZrO₂

The activity test results are summarized in Figure 6. 2Pd/ZrO₂ led to mainly C1 products (including methanol, methane, CO and CO₂) resulting from C-C bond cleavage. The C-O to C-C bond cleavage ratio of 2Pd/ZrO₂ is as low as 0.3. By doping of WO₃, the selectivity to C1 products decreased from 77% to 41% while the selectivity to ethanol was increased from 15% to

48%. The C-O to C-C bond cleavage ratio increased from 0.3 to 1.52 suggesting that WO_3 significantly changed the reaction pathway of aqueous phase HDO of ethylene glycol. The C-O bond cleavage relies heavily on the presence of WO_3 . Doping of WO_3 enhances the C-O bond cleavage and suppresses the C-C bond cleavage over Pd/ZrO_2 in aqueous phase HDO of ethylene glycol.

Figure 7 Ethanol TPD profile of 2Pd/ZrO_2

Figure 8 Ethanol TPD profile of $\text{WO}_3\text{-ZrO}_2$

Figure 9 Ethanol TPD profile of 2Pd/WO₃-ZrO₂

The doping of WO₃ onto the ZrO₂ introduced a large amount of Brönsted acidic sites to ZrO₂ and the resultant Pd/WO₃-ZrO₂ as evidenced by IR-py spectra (Figure 2). Ethanol was employed as the probe molecule to study the adsorption of reactant molecules on the catalysts (Figure 7-Figure 9). Figure 7 shows that ethanol desorbed as molecular ethanol at temperature below 100 °C on 2Pd/ZrO₂. The evolution of H₂O and ethylene were observed at about 110 °C and 225 °C respectively. This suggests that the dehydration of ethanol took place at approximately 110 °C and the resultant ethylene desorbed at 225 °C. The evolution of acetaldehyde and H₂ at about 340 °C was observed. Further increasing the temperature, the adsorbed species decomposed into CH₄ and CO at about 415 °C. For WO₃-ZrO₂, there are two desorption features of ethanol (Figure 8). The low-temperature desorption feature at 97 °C corresponds to the bound ethanol molecules in excess of one per acidic site [27]. The high-temperature feature at about 219 °C corresponds to stoichiometric adsorption of ethanol molecules on Brönsted acidic sites [27]. The dehydration of adsorbed ethanol on WO₃-ZrO₂ occurred at 277 °C as indicated by the simultaneous evolution of ethylene and H₂O. No significant acetaldehyde evolution was observed on WO₃-ZrO₂. The impregnation of palladium seems attenuate the strength of these ethanol adsorption sites on WO₃-ZrO₂ since the high-temperature desorption feature of ethanol at 219 °C

on $\text{WO}_3\text{-ZrO}_2$ (Figure 8) is not present on $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$ (Figure 9). There are two distinct peaks of mass spectra sign m/z 28 at 219 °C and 348 °C along with the evolution of H_2 for $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$. The peak at 219 °C corresponds to ethylene possibly from ethanol dehydration. The dehydration temperature is much lower on $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$ (<200 °C) than that on $\text{WO}_3\text{-ZrO}_2$ (~277 °C). The peak at 348 °C corresponds to CO evolution due to the decomposition of some strongly adsorbed species resulted from the dissociative adsorption of ethanol (similar decomposition peak was observed in acetaldehyde TPD, Figure S1). It suggests that the highly selective hydrodeoxygenation over $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$ results from the complex and synergic effect of palladium and WO_3 . To summarize, WO_3 introduces Brönsted acidic sites to Pd/ZrO_2 and the acidity of $\text{WO}_3\text{-ZrO}_2$ is somehow attenuated by palladium.

4.2 Interaction between palladium and WO_3

Figure 10 Effect of palladium particle size on the reaction rates and selectivity

Catalysts: $\text{Pd}/\text{WO}_3\text{-ZrO}_2$ with 0.5-2 wt.% Pd; Carbon balance: $100\pm 2\%$; Conversion: ~5%, Feed: 10 wt.% ethylene glycol. $T=240$ °C, $P=1050$ psig, $\text{WHSV}=0.25\text{-}0.7$ $\text{g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$;

$\text{Pd}/\text{WO}_3\text{-ZrO}_2$ catalysts with various Pd particle sizes were prepared and studied to understand the interaction between palladium and WO_3 in $\text{Pd}/\text{WO}_3\text{-ZrO}_2$. The C-O and C-C bond

cleavage rates were derived from the generation rates of corresponding C-O and C-C cleavage products based on per mole of accessible palladium on the catalyst surface. The reaction rates of ethylene glycol, the cleavage rates of C-O and C-C bonds as well as the C-O/C-C ratios are summarized in Figure 10. The rates of C-O and C-C bond cleavage increase with increasing palladium particle size without significantly changing the selectivity. The diffuse reflectance UV-vis absorption spectra showed that the WO_3 domain size increases with the increasing palladium particle size (Figure 3). This indicates that there is strong interaction between Pd particles and $\text{WO}_3\text{-ZrO}_2$.

Figure 11 Isopropylamine TPD profiles of catalysts

Figure 12 NH_3 evolution during isopropylamine TPD

Activity tests show that ZrO_2 is inactive for the aqueous phase HDO of ethylene glycol under

the experimental conditions. Although $\text{WO}_3\text{-ZrO}_2$ led to the high selectivity to acetaldehyde, it deactivated after 8 h time-on-stream due to the severe coke deposition (Figure S2). Acetaldehyde was possibly produced by the dehydration of ethylene glycol over acidic sites. Temperature programmed desorption of isopropylamine (isopropylamine-TPD) was employed to characterize the nature of the acidic sites (Figure 11). $\text{WO}_3\text{-ZrO}_2$ has stronger acidic sites which led to the high-temperature region desorption of isopropylamine. Those stronger acidic sites of $\text{WO}_3\text{-ZrO}_2$ are prone to coke formation (Figure S2). Such strong acidic sites disappear after impregnation of palladium, leading to improved catalyst stability as evidenced by only slight decrease in ethylene glycol conversion (12.1% vs. 13.9%) after 8 h time-on-stream. It indicates that the presence of both palladium and WO_3 is crucial for the selective hydrodeoxygenation of ethylene glycol.

Isopropylamine is known to form 1:1 complex with Brönsted acidic sites and decompose to propene and ammonia at temperatures between 302 °C and 377 °C, in a reaction analogous to solution-phase Hoffmann elimination [27, 28]. The decomposition of isopropylamine led to simultaneous evolution of propene and NH_3 (Figure S3). Figure 12 shows the NH_3 evolution profiles of the catalysts during the isopropylamine-TPD. The decomposition temperature of isopropylamine over $\text{WO}_3\text{-ZrO}_2$ is about 360 °C which is consistent with literature [27, 28]. However the introduction of palladium significantly lowers the decomposition temperature of isopropylamine as evidenced by the evolution of NH_3 at a much lower temperature. Although the 2Pd/ZrO_2 is capable of decomposing isopropylamine to ammonia at temperatures below 300 °C, the presence of both Pd and WO_3 largely enhances the decomposition as evidenced by the intensive NH_3 evolution signal over $\text{Pd/WO}_3\text{-ZrO}_2$ catalysts. This strongly suggests a synergic effect between palladium and WO_3 . Different from $\text{WO}_3\text{-ZrO}_2$, however, only a small amount of

propene was detected during isopropylamine decomposition over Pd/WO₃-ZrO₂ (Figure S4), likely due to the strong adsorption or polymerization on Pd [29, 30]. The high temperature desorption feature of isopropylamine above 200 °C over WO₃-ZrO₂ is not present on Pd/WO₃-ZrO₂ catalysts (Figure 11) possibly due to the strong acidic sites being blocked by Pd particles. The deposition of Pd on these strong acidic sites could induce an electronic interaction between Pd and WO₃-ZrO₂ [21, 31] which in turn modifies the acidity and reducibility of the Pd/WO₃-ZrO₂ catalysts [32, 33]. As a result, a synergic effect between palladium and WO₃ facilitates the elimination of NH₃ from isopropylamine. Such an elimination process could be similar to the elimination of H₂O from polyols in aqueous phase HDO process.

4.3 Aqueous phase HDO mechanism of ethylene glycol

Scheme 1 Direct hydrogenolysis reaction pathway

Scheme 2 Dehydration-hydrogenation reaction pathway

With both palladium and WO₃, hydrodeoxygenation of ethylene glycol and resultant alcohols could proceed via either direct hydrogenolysis of C-O bonds or a dehydration-hydrogenation pathway. Isotope-labelled experiments were designed to obtain more direct evidence on the aqueous phase HDO pathway of ethylene glycol. Deuterated ethylene glycol (DOCH₂CH₂OD) was employed instead of its non-deuterated counterpart in the tests. These isotope-labelled experiments were conducted with D₂O as solvent and H₂ as the hydrogen source at the same reaction temperature and pressure used in the previous activity tests.

Table 2 Composition of deuterated ethylene glycol in D₂O after reaction with H₂

Ethylene Glycol	WO ₃ -ZrO ₂	2Pd/WO ₃ -ZrO ₂
	mol%	mol%
DOCH ₂ CH ₂ OD	96.0	27.9
DOCH ₂ CHDOD	1.0	17.5
DOCHDCHDOD	2.3	42.7
DOCD ₂ CH ₂ OD	0.6	12.0

Table 3 Composition of deuterated ethanol products

Ethanol ^a	WO ₃ -ZrO ₂	2Pd/WO ₃ -ZrO ₂
	mol%	mol%
DOCH ₂ CH ₃ /DOCH ₂ CH ₂ D/DOCH ₂ CHD ₂ /DOCH ₂ CD ₃	100	34.1
DOCHDCH ₃ /DOCHDCH ₂ D/DOCHDCHD ₂ /DOCHDCHD ₂ CD ₃	0	67.5
DOCD ₂ CH ₃ /DOCD ₂ CH ₂ D/DOCD ₂ CHD ₂ /DOCD ₂ CD ₃	0	6.5

^a Produced from the HDO of deuterated ethylene glycol in D₂O with H₂.

Table 4 Composition of deuterated methanol products

Methanol ^a	WO ₃ -ZrO ₂	2Pd/WO ₃ -ZrO ₂	2Pd/WO ₃ -ZrO ₂ ^b
	mol%	mol%	mol%
<u>C</u> H ₃ OD	0	11.1	0.6
<u>C</u> DH ₂ OD	0	31.4	1.6
<u>C</u> D ₂ HOD	0	38.0	13.7
<u>C</u> D ₃ OD	0	19.5	84.0

^a Produced from the HDO of deuterated ethylene glycol in D₂O with H₂.

^b H-D scrambling using 10 wt.% CD₃OH in H₂O and H₂ as the feeding.

The hypothesis is that if hydrodeoxygenation proceeds via direct hydrogenolysis of ethylene glycol, both the ethanol and methanol produces from deuterated ethylene glycol in D₂O should have zero or one D on their methyl group due to the scrambling of H on metal by D from D₂O (Scheme 1). If there are more than one D on the methyl groups in ethanol or methanol, the D should be a result of direct H-D exchange on metal. On the other hand, if the hydrodeoxygenation proceeds via a dehydration and hydrogenation pathway, vinyl alcohol (CH₂=CHOD) should be the primary dehydration product of ethylene glycol. Isomerization of vinyl alcohol to acetaldehyde involves the hydrogen transfer from an –OD group to the methylene group of a vinyl alcohol leading to an acetaldehyde intermediate with a deuterated methyl group (CH₂DCHO). However, both direct hydrogenation of vinyl alcohol and the resultant acetaldehyde from vinyl alcohol isomerization should lead to ethanol with both deuterated methyl and methylene groups (CH₂DCHDOD) (Scheme 2).

Table 2 summarizes the H-D scrambling results of ethylene glycol after the HDO tests. Table 3 summarizes the composition of HDO products of ethanol. Interestingly, very limited H-D scrambling of $\text{DOCH}_2\text{CH}_2\text{OD}$ (~4%) was observed over $\text{WO}_3\text{-ZrO}_2$. The majority of the ethylene glycol ($\text{DOCH}_2\text{CH}_2\text{OD}$) remained untouched. Dehydration followed by isomerization lead to a deuterated methyl group on ethanol. No C-C bond hydrogenolysis product (methanol) over $\text{WO}_3\text{-ZrO}_2$ was observed. This confirms that the acidic sites on $\text{WO}_3\text{-ZrO}_2$ favor the dehydration of ethylene glycol.

Compared to $\text{WO}_3\text{-ZrO}_2$, more than 70% of remaining ethylene glycol (Table 2) has experienced H-D scrambling over $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$ during the test. However, the H-D scrambling of ethylene glycol over $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$ could either proceed via the dehydration-hydration pathway or direct H-D scrambling over metallic sites. Deuterated methanol (CD_3OH) in H_2O was employed to evaluate the direct H-D scrambling over $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$ during the aforementioned aqueous phase HDO conditions with H_2 . Table 4 summarizes the composition of methanol from HDO and the H-D scrambling results of deuterated methanol. Methanol dehydration can only proceed between hydroxyl groups of two methanol molecules to form the dimethyl ether (CD_3OCD_3). Hydrolysis of the resultant dimethyl ether in H_2O will form CD_3OH and no H-D scrambling on methyl group is possible. If there is only H-D scrambling of the $-\text{CD}_3$ group of methanol, it must proceed over the metallic sites of $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$. Table 4 shows that only about 16% of the CD_3OH has experience H-D scrambling, much less than the H-D scrambling of ethylene glycol (>70%) over $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$ (Table 2). This suggests that the dehydration-hydration followed by hydrogenation pathway prevails over hydrogenolysis of ethylene glycol during aqueous phase HDO over $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$.

Table 3 also shows that 70% of the ethanol produced over 2Pd//WO₃-ZrO₂ has deuterated methylene groups (-CHD- / -CD₂-) which suggest that the majority of ethanol is produced by dehydration-hydrogenation of ethylene glycol (DOCH₂CH₂OD). Thus the high degree H-D scrambling of the remained ethylene glycol and resultant ethanol, methanol products over 2Pd//WO₃-ZrO₂ suggests that the dehydration step over 2Pd//WO₃-ZrO₂ is in equilibrium and not the rate-limiting step of HDO. In summary, the aqueous phase HDO of ethylene glycol proceeds via the dehydration-hydrogenation reaction pathway over the bifunctional 2Pd//WO₃-ZrO₂ and hydrogenation of the dehydration products shifts the dehydration-hydration equilibrium towards the dehydration direction.

5. CONCLUSIONS

The strong interaction between metallic and acidic sites of 2Pd//WO₃-ZrO₂ is required to efficiently remove oxygen from sugars to form mono-functional oxygenates in aqueous phase HDO. Aqueous phase HDO of ethylene glycol proceeds via a dehydration-hydrogenation pathway on 2Pd//WO₃-ZrO₂ with the dehydration step being in equilibrium. Hydrogenation of dehydration products shifts the equilibrium toward the dehydration direction, leading to selective cleavage of C-O. A fundamental understanding on the aqueous phase HDO mechanism and the interaction between the metal and acid sites will help develop more efficient bifunctional catalysts for this process.

ACKNOWLEDGMENTS

We would like to acknowledge Virent for their initial work on Pd//WO₃-ZrO₂ for HDO of polyols,

especially Dr. Randy Cortright, Ms. Liz Woods and Mr. Brian Blank from Virent for numerous invaluable discussions and suggestions. We also acknowledge the financial support from the National Advanced Biofuels Consortium (NABC) which is funded by the Department of Energy's Office of Biomass Program with recovery act funds, as well as the financial support by the U.S. Department of Energy (grant No. DE-FG02-05ER15712). The Pacific Northwest National Laboratory is operated by Battelle for the United States Department of Energy under Contract DE-AC05-76RL01830. We thank Berlin Sudduth (WSU) for reading through the paper.

REFERENCES

- [1] G.W. Huber, B.E. Dale, *Sci.Am.*, 301 (2009) 52-56.
- [2] J.C. Serrano-Ruiz, R. Luque, A. Sepulveda-Escribano, *Chem. Soc. Rev.*, 40 (2011) 5266-5281.
- [3] D. Mohan, C.U. Pittman, P.H. Steele, *Energy Fuels*, 20 (2006) 848-889.
- [4] C. Liu, H. Wang, A.M. Karim, J. Sun, Y. Wang, *Chem. Soc. Rev.*, 43 (2014) 7594-7623.
- [5] G.W. Huber, S. Iborra, A. Corma, *Chem. Rev.*, 106 (2006) 4044-4098.
- [6] Y. Sun, J. Cheng, *Bioresour. Technol.*, 83 (2002) 1-11.
- [7] J.-P. Lange, *Biofpr.*, 1 (2007) 39-48.
- [8] E.L. Kunkes, D.A. Simonetti, R.M. West, J.C. Serrano-Ruiz, C.A. Gärtner, J.A. Dumesic, *Science*, 322 (2008) 417-421.
- [9] L. Chen, Y. Zhu, H. Zheng, C. Zhang, B. Zhang, Y. Li, *J. Mol. Catal. A: Chem.*, 351 (2011) 217-227.
- [10] G.W. Huber, R.D. Cortright, J.A. Dumesic, *Angew. Chem. Int. Ed.*, 43 (2004) 1549-1551.
- [11] N.I. Pehlivanoglu, H. Uslu, S.I.s.l. Kirbaşlar, *J. Chem. Eng. Data*, 55 (2010) 2970-2973.

- [12] L. Vilcocq, A. Cabiach, C. Especel, S. Lacombe, D. Duprez, *Catal. Today*, 189 (2012) 117-122.
- [13] N. Li, G.A. Tompsett, T. Zhang, J. Shi, C.E. Wyman, G.W. Huber, *Green Chemistry*, 13 (2011) 91-101.
- [14] C.D. Baertsch, K.T. Komala, Y.-H. Chua, E. Iglesia, *J. Catal.*, 205 (2002) 44-57.
- [15] D. Barton, S. Soled, E. Iglesia, *Top. Catal.*, 6 (1998) 87-99.
- [16] D.G. Barton, M. Shtein, R.D. Wilson, S.L. Soled, E. Iglesia, *J. Phys. Chem. B*, 103 (1999) 630-640.
- [17] G. Larsen, E. Lotero, L.a.M. Petkovic, D.S. Shobe, *J. Catal.*, 169 (1997) 67-75.
- [18] T.K. Phung, L. Proietti Hernández, G. Busca, *Appl. Catal., A: General*, 489 (2015) 180-187.
- [19] S.-H. Chai, B. Yan, L.-Z. Tao, Y. Liang, B.-Q. Xu, *Catal. Today*, 234 (2014) 215-222.
- [20] W. Dedsuksophon, K. Faungnawakij, V. Champreda, N. Laosiripojana, *Bioresour. Technol.*, 102 (2011) 2040-2046.
- [21] O.G. Marin-Flores, A.M. Karim, Y. Wang, *Catal. Today*, 237 (2014) 118-124.
- [22] G. Bergeret, P. Gallezot, Particle Size and Dispersion Measurements, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.) *Handbook of Heterogeneous Catalysis*, Wiley-VCH Verlag GmbH & Co. KGaA2008.
- [23] E.P. Parry, *J. Catal.*, 2 (1963) 371-379.
- [24] G.K. Chuah, S. Jaenicke, T.H. Xu, *Surf. Interface Anal.*, 28 (1999) 131-134.
- [25] R. Kourieh, S. Bennici, A. Auroux, *React. Kinet., Mech. Catal.*, 105 (2012) 101-111.
- [26] K.K. Ramasamy, Y. Wang, *J. Energy Chem.*, 22 (2013) 65-71.
- [27] W.E. Farneth, R.J. Gorte, *Chem. Rev.*, 95 (1995) 615-635.
- [28] T.J.G. Kofke, R.J. Gorte, W.E. Farneth, *J. Catal.*, 114 (1988) 34-45.

- [29] E.I. Altman, *Surf. Sci.*, 547 (2003) 108-126.
- [30] T. Perger, T. Kovács, T. Turányi, C. Treviño, *Combust. Flame*, 142 (2005) 107-116.
- [31] P. Vijayanand, K. Chakarova, K. Hadjiivanov, P. Lukinskas, H. Knozinger, *Phys. Chem. Chem. Phys.*, 5 (2003) 4040-4044.
- [32] M. Occhiuzzi, D. Cordischi, S. De Rossi, G. Ferraris, D. Gazzoli, M. Valigi, *Appl. Catal., A: General*, 351 (2008) 29-35.
- [33] X. Wu, L. Zhang, D. Weng, S. Liu, Z. Si, J. Fan, *J. Hazard. Mater.*, 225–226 (2012) 146-154.

Table list:

Table 1 Physicochemical properties of the supports and catalysts

Table 2 Composition of deuterated ethylene glycol in D₂O after reaction with H₂

Table 3 Composition of deuterated ethanol products

Table 4 Composition of deuterated methanol products

Table 1 Physicochemical properties of the supports and catalysts

Sample	Pd loading wt. %	W loading wt. %	Surface area $\text{m}^2 \cdot \text{g}^{-1}$	Pore volume $\text{cm}^3 \cdot \text{g}^{-1}$	Pulse chemisorption. CO/Pd	Pd particle size ^a nm
ZrO ₂	-	-	99	0.30	-	-
2Pd/ZrO ₂	2.0	-	101	0.31	0.86	1.30
WO ₃ -ZrO ₂	-	12.5	116±2	0.23	-	-
2Pd/WO ₃ -ZrO ₂	2.0	12.5	110±2	0.22	0.17	6.73
1.0Pd/WO ₃ -ZrO ₂	1.0	12.5	-	-	0.45	2.46
0.5Pd/WO ₃ -ZrO ₂	0.50	12.5	-	-	0.70	1.60

^a palladium particle sizes were estimated by $D=6(v_m/a_m)/d_{VA}$ [22], where D is the metal dispersion, d_{VA} is the mean particle size in angstrom, $v_m = 14.70 \text{ \AA}^3$ is the volume occupied by a Pd atom in bulk metal, $a_m = 7.93 \text{ \AA}^2$ is the area occupied by a surface Pd atom.

Table 2 Composition of deuterated ethylene glycol in D₂O after reaction with H₂

Ethylene Glycol	WO ₃ -ZrO ₂	2Pd/WO ₃ -ZrO ₂
	mol%	mol%
DOCH ₂ CH ₂ OD	96.0	27.9
DOCH ₂ CHDOD	1.0	17.5
DOCHDCHDOD	2.3	42.7
DOCD ₂ CH ₂ OD	0.6	12.0

Table 3 Composition of deuterated ethanol products

Ethanol ^a	WO ₃ -ZrO ₂ mol%	2Pd/WO ₃ -ZrO ₂ mol%
DOCH ₂ CH ₃ /DOCH ₂ CH ₂ D/DOCH ₂ CHD ₂ /DOCH ₂ CD ₃	100	34.1
DOCHDCH ₃ /DOCHDCH ₂ D/DOCHDCHD ₂ /DOCHDCHD ₂	0	67.5
DOCD ₂ CH ₃ /DOCD ₂ CH ₂ D/DOCD ₂ CHD ₂ /DOCD ₂ CD ₃	0	6.5

^a Produced from the HDO of deuterated ethylene glycol in D₂O with H₂.

Table 4 Composition of deuterated methanol products

Methanol ^a	WO ₃ -ZrO ₂	2Pd/WO ₃ -ZrO ₂	2Pd/WO ₃ -ZrO ₂ ^b
	mol%	mol%	mol%
<u>C</u> H ₃ OD	0	11.1	0.6
<u>C</u> DH ₂ OD	0	31.4	1.6
<u>C</u> D ₂ HOD	0	38.0	13.7
<u>C</u> D ₃ OD	0	19.5	84.0

^a Produced from the HDO of deuterated ethylene glycol in D₂O with H₂.

^b H-D scrambling using 10 wt.% CD₃OH in H₂O and H₂ as the feeding.

Figure list

Figure 1 XRD spectra of a) $\text{WO}_3\text{-ZrO}_2$ and b) $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$

Figure 2 IR-Py spectra of a) ZrO_2 , b) $\text{WO}_3\text{-ZrO}_2$, c) $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$

Reduced at 300 °C for 1 h, spectra collected at 150 °C

Figure 3 Diffuse Reflectance UV-vis absorption spectra of $\text{WO}_3\text{-ZrO}_2$ a) without palladium, b) Pd particle size of 1.48 nm, c) Pd particle size of 2.03 nm.

Figure 4 Products distribution with/without WO_3

Feed: 10 wt.% ethylene glycol, $T=240^\circ\text{C}$, $P=1050$ psig, $\text{H}_2/\text{C}=2$, $\text{WHSV}=1.10\text{ g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for $2\text{Pd}/\text{ZrO}_2$ and $0.23\text{ g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$

Figure 5 Products distribution over $\text{Pd}/\text{WO}_3\text{-ZrO}_2$ catalysts of different Pd particle size

Catalysts: $\text{Pd}/\text{WO}_3\text{-ZrO}_2$ with 0.5 wt.%, 1 wt.% and 2 wt.% Pd loadings corresponding to 1.60, 2.46 and 6.73 nm Pd particle sizes, respectively; Carbon balance: $100\pm 2\%$; Feed: 10 wt.% ethylene glycol. $T=240^\circ\text{C}$, $P=1050$ psig, $\text{WHSV}=0.25\text{-}0.7\text{ g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$;

Figure 6 Comparison of the selectivity to C-O and C-C bond cleavage

Feed: 10 wt.% Ethylene glycol, $T=240^\circ\text{C}$, $P=1050$ psig, $\text{H}_2/\text{C}=2$, $\text{WHSV}=1.10\text{ g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for $2\text{Pd}/\text{ZrO}_2$ and $0.23\text{ g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$

Figure 7 Ethanol TPD profile of $2\text{Pd}/\text{ZrO}_2$

Figure 8 Ethanol TPD profile of $\text{WO}_3\text{-ZrO}_2$

Figure 9 Ethanol TPD profile of $2\text{Pd}/\text{WO}_3\text{-ZrO}_2$

Figure 10 Effect of palladium particle size on the reaction rates and selectivity

Catalysts: $\text{Pd}/\text{WO}_3\text{-ZrO}_2$ with 0.5-2 wt.% Pd; Carbon balance: $100\pm 2\%$; Conversion: $\sim 5\%$, Feed: 10 wt.% ethylene glycol. $T=240^\circ\text{C}$, $P=1050$ psig, $\text{WHSV}=0.25\text{-}0.7\text{ g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$;

Figure 11 Isopropylamine TPD profiles of catalysts

Figure 12 NH_3 evolution during isopropylamine TPD

Scheme 1 Direct hydrogenolysis reaction pathway

Scheme 2 Dehydration-hydrogenation reaction pathway

Figure S1. Acetaldehyde TPD of $\text{Pd}/\text{WO}_3\text{-ZrO}_2$

Figure S2. Thermogravimetric analysis of spent catalysts

Scheme 1

Scheme 2

Graphic abstract