



Role of tungsten in the aqueous phase hydrodeoxygenation of ethylene glycol on tungstated zirconia supported palladium



Oscar G. Marin-Flores^a, Ayman M. Karim^{b,*}, Yong Wang^{a,b,*}

^a The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164, United States

^b Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA 99352, United States

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ABSTRACT

The focus of the present work was specifically on the elucidation of the role played by tungsten on the catalytic activity and selectivity of tungstated zirconia supported palladium (Pd-mWZ) for the aqueous phase hydrodeoxygenation (APHDO) of ethylene glycol (EG). Zirconia supported palladium (Pd-mZ) was used as reference. The catalysts were prepared via incipient wet impregnation and characterized using X-ray diffraction (XRD), temperature-programmed reduction (TPR), CO pulse chemisorption, CO-DRIFTS, ammonia temperature-programmed desorption (NH₃-TPD) and pyridine adsorption. The presence of W results in larger Pd particles on supported Pd catalysts, i.e., 0.9 and 6.1 nm Pd particles are for Pd-mZ and Pd-mWZ, respectively. The catalytic activity measurements show that the overall intrinsic activity of Pd particles on mWZ is 1.9 times higher than on mZ. APHDO process appears to be highly favored on Pd-mWZ whereas Pd-mZ exhibits a higher selectivity for reforming. This difference in terms of selectivity seems to be related to the high concentration of Brønsted acid sites and electron-deficient Pd species present on Pd-mWZ.

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1. Introduction

The upcoming fossil fuel shortage demands the development of not only economical but also efficient new technologies for the production of synthetic fuels from renewable resources such as plant biomass. Lignocellulose is a generic term used to describe a type of inexpensive and abundant non-edible biomass that can be found in most plants. The catalytic conversion of lignocellulosic biomass to fuels and chemicals has attracted a great deal of attention as it is considered a technology with the potential to attenuate global warming and build up a low carbon society [1–3]. However, some factors such as the inherent complexity and heterogeneous composition of this type of biomass present a series of challenges that need to be overcome before this technology becomes widely used.

Aqueous phase processing (APP) is a promising technology for the conversion of aqueous biomass-derived feedstocks to chemicals and fuels [4–6]. The major advantage of this approach lies in the ability to selectively produce targeted products by carefully controlling the processes taking place in the aqueous phase. Sugar alcohols include polyols derived from the APP of lignocellulosic

biomass. These compounds are used as precursors to plastics, surfactants and medicines as well as low-calorie and non-cariogenic sweeteners [7]. Aqueous-phase hydrodeoxygenation (APHDO) is a post processing step of the APP, and involves the conversion of oxygenated molecules into alkanes by a series of dehydration and hydrogenation steps [8–10]. APHDO processes require bifunctional catalysts with both metallic and acidic sites. Oxygen is removed from the feedstock molecules through C–O bond cleavage reactions on either metallic or acidic sites. Subsequently, hydrogen is added to the oxygen-deficient molecules by hydrogenation over the metallic sites. Bifunctional catalysts such as palladium-promoted tungstated zirconia (WZ) have been found to be active and selective for a variety of reactions [11–14], showing potential for industrial applications. However, differences in terms of preparation and crystalline structure may lead to significant changes in the acidity and catalytic properties of this material. Consequently, it is difficult to use previous works as reference for new studies, unless the number of variables involved in the synthesis method is minimized. To our best knowledge, the use of this catalyst for the APHDO of sugar alcohols has not been extensively investigated. Thus, the aim of the present work is to specifically study the role played by tungsten on the structure and catalytic properties of a tungstated zirconia-supported palladium catalyst for the APHDO of a model sugar alcohol such as ethylene glycol. To achieve this, a series of catalysts with similar crystalline structure were prepared employing

* Corresponding authors.

E-mail addresses: ayman.karim@pnnl.gov, omarinflores@hotmail.com (A.M. Karim), wang42@wsu.edu (Y. Wang).

a simple preparation method such as dry impregnation, and subsequently tested under the same operating conditions. In doing so, the role played by tungsten can be elucidated in a more straightforward manner.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared using monoclinic zirconia purchased from Saint-Gobain Nor-Pro as starting material. Ammonium metatungstate hydrate ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$) and tetramminepalladium (II) nitrate $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_6$ purchased from Alfa Aesar were used as tungsten (W) and palladium (Pd) precursors, respectively. Tungstated zirconia was prepared via incipient wetness impregnation of an aqueous solution of W precursor on monoclinic zirconia to obtain a nominal loading of 12.5 wt.%, which is slightly higher than the required to form a monolayer of tungsten-containing species on the surface of the monoclinic zirconium support (12.1 wt.%) [15]. After each impregnation step the catalyst was dried at 393 K. Once the set of impregnations was completed, the catalysts were calcined in static air at 673 K for 6 h, using a ramping rate of 2 K min^{-1} . A similar procedure was followed with Pd to obtain a nominal loading of 2 wt.%.

2.2. Characterization

Textural properties were measured using a Micromeritics TriStar II 3020 Automatic Physisorption Analyzer. Prior to analysis, the samples were degassed under vacuum for 2 h at 393 K. The crystalline structure of the samples was determined with a Philips diffractometer with Co K α radiation, iron filter, and Bragg–Brentano optical configuration. Temperature-programmed reductions and pulse CO chemisorption experiments were carried out using a Micromeritics AutoChem II 2920 Chemisorption Analyzer with a TCD detector and also connected to a Pfeiffer ThermoStar Quadrupole Mass Spectrometer. For ammonia (NH_3) temperature-programmed desorption experiments, the samples were first reduced with a mixture 10% H_2 /Ar at 573 K for 1 h, using a ramping rate of 10 K min^{-1} . Ammonia (10% NH_3 /Ar) was adsorbed by the sample at room temperature for 1 h, after which the desorption profile was obtained under helium using a ramping rate of 10 K min^{-1} and recording the amount of ammonia desorbed with the mass spectrometer. For the pulse CO chemisorption experiments, samples of about 0.1 g (60–100 mesh) were loaded in the instrument and heated under hydrogen to 573 K at 2.5 K min^{-1} and then reduced at the same temperature with 30 sccm of H_2 for 1 h. Next, the samples were cooled down to 313 K with 20 sccm of He and purged for 1 h before CO titration, which was performed with 10% CO in He. Two series of injections were carried out using the same procedure. CO chemisorbed was calculated as the difference between the CO uptakes of these two series of injections.

A Bruker Tensor 27 FTIR was used to run DRIFTS. This instrument was equipped with a Praying Mantis accessory for studies under controlled environments. For CO-DRIFTS, the samples were first reduced in a mixture 10% H_2 /Ar for 1 h using a ramping rate of 10 K min^{-1} . Backgrounds were collected under helium at different temperatures. CO adsorption at 298 K was performed by feeding a mixture of 5 sccm of 10% CO/He and 50 sccm of helium. A set of spectra were collected to determine if the adsorption of CO was no longer changing with time. To ensure saturation of the sample with CO, the flow of helium was stopped and a second stage of CO adsorption was initiated for another period of 15 min. The evacuation of the reaction chamber was performed using 50 sccm of pure helium.

Pyridine-DRIFTS were carried out using a similar procedure as the one used for CO, with exception of the adsorption step, which was performed for 30 min using a flow 5 sccm of He saturated with pyridine vapor.

2.3. Activity tests

The catalytic activity of the samples was measured using a 300-mL Parr batch reactor. The reaction temperature was set to 523 K. Ethylene glycol diluted in water (10 vol.%) was used as reaction mixture. The volume introduced into the reactor was 50 mL and the agitation speed was set to 400 rpm. To start, 0.5 g of catalyst was pretreated in a tube furnace using pure hydrogen at 573 K for 1 h. Once the sample was cooled to room temperature, the as-pretreated samples were rapidly introduced under flowing nitrogen into the glass liner containing the liquid reaction mixture. The reactor was immediately sealed and pressurized at room temperature with 1000 psi (approx. 6.9 MPa) of a mixture of 80% H_2 and 20% N_2 (N_2 was used as an internal standard for GC analysis). After 5 h of reaction, the agitator was stopped and the reactor was immersed in a chilling bath (water/ice, 273 K) to prevent further reaction before analysis. Both gas and liquid products were analyzed using an Agilent 7890A Gas Chromatograph equipped with TCD and FID detectors. Molecular sieve 13 \times and Haysep D packed columns combined with a methanizer for CO and CO_2 detection were used for the detection of gas products. The analysis of the liquid phase was performed with a HPFFAP capillary column and using acetonitrile as internal standard.

The operating conditions were selected to eliminate gas–liquid mass transfer issues and make sure that the reaction rates are limited only by the solubility of H_2 in the liquid phase. To do so, the gas/liquid volumetric mass-transfer coefficient $k_{L,a}$ in s^{-1} was first calculated using the equation: $k_{L,a} = 3 \times 10^{-7} N^{3.6}$ [16], where N represents the agitator speed in s^{-1} . This empirical equation has been deduced from experimental data obtained in hydrogenation reactors using similar operating conditions. Next, the H_2 mass transfer rates were estimated according to: $r_{\text{H}_2,\text{MT}} = k_{L,a}(C_{\text{H}_2,\text{G}} - C_{\text{H}_2,\text{L}})$, where $C_{\text{H}_2,\text{G}}$ and $C_{\text{H}_2,\text{L}}$ represent the concentration of H_2 in the gas (2.22 mol L^{-1}) and in the liquid phase (0.13 mol L^{-1}), respectively. The maximum rate of reaction $r_{\text{H}_2,\text{RXN}}$ was calculated assuming a conversion of 100% and a stoichiometry ratio H_2/EG of 2. Following this procedure, the value obtained for $r_{\text{H}_2,\text{RXN}}$ was 10^{-4} mol L^{-1} s^{-1} , whereas that calculated for $r_{\text{H}_2,\text{MT}}$ was 0.43 mol L^{-1} s^{-1} . Hence, the ratio $r_{\text{H}_2,\text{MT}}/r_{\text{H}_2,\text{RXN}}$ was 4300 $\gg 1$ and, therefore, no gas–liquid mass transfer problems were found in the system.

Another possible issue in the reactor may be related to the presence of mass transport limitations between the solid catalyst particles and the liquid phase. However, the stirring rate used in the experiments (400 rpm) was selected to prevent phase segregation and to obtain perfect mixing, which is expected to minimize solid–liquid mass transport limitations.

3. Results and discussion

3.1. Characterization

3.1.1. Physicochemical properties

The results obtained from physisorption and chemisorption analysis are summarized in Table 1. The addition of Pd to monoclinic zirconia mZ led to minor changes in surface area and pore volume, i.e., from 99 to 98 m^2 g^{-1} and from 0.30 to 0.29 cm^3 g^{-1} , respectively. However, the impregnation of tungsten on the mZ support resulted in more significant changes on the catalyst structure, with surface area of 94 m^2 g^{-1} and pore volume of 0.24 cm^3 g^{-1} . The

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