Supported Metal Oxide Catalysts in the Conversion of Oxygenates

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Abstract

Metal oxides are widely utilized as heterogeneous catalysts and catalyst supports and have been used recently for the on-purpose production of commodity chemicals through the conversion of biorenewable oxygenated feedstocks such as ethanol and carboxylic acids. The first part of this work focuses on multifunctional Lewis acid catalysts as effective ethanol-to-butadiene catalysts. Promoted with Ag-SiO₂ in a physical mixture, oxides of four elements, Ta, Y, Pr, and La were tested on two different supports, crystalline Beta zeolite (HBZ) and amorphous SiO₂, in the cascade reaction of ethanol to butadiene. Results from diffuse reflectance UV-Vis spectroscopy showed zeolite-supported Ta and Pr catalysts have a smaller metal oxide cluster size relative to their SiO_2 analogues. The oxidation states of the cations supported on HBZ, evaluated by X-ray photoelectron spectroscopy (XPS), were the same as their SiO₂-supported analogues. Comparison of the performance of SiO₂-supported catalysts revealed a greater distribution of butadiene among the C4 coupling products over stronger Lewis acids, such as Ta, which was evaluated by the 2propanol decomposition reaction to propene and acetone. The use of Beta zeolite as a support for the Lewis acid cations significantly enhanced the rate of C-C coupling by order of magnitude greater than their SiO₂ analogues.

The second part of the work focuses on supported tungsten oxide (WO_x), a reducible metal oxide. When promoted with Pd, supported WO_x catalysts can be used in the reduction of carboxylic acids with H₂ to form aldehydes and alcohols. During this reaction, hydrogen spillover from Pd nanoparticles may participate in the reaction itself while also facilitating the reduction of the WO_x species. The influence of hydrogen spillover on SiO₂ and P25-TiO₂ supported WO_x species was studied through a variety of techniques. Results from H₂ temperature-programmed reduction showed the presence of Pd on SiO₂-supported WO_x lowered the initial reduction temperature of the WO_x species but did not affect the reduction of those species supported on TiO₂. Highly isolated WO_x species on acid-treated SiO₂ were less reducible than larger WO_x clusters on SiO₂. High-angle annular dark-field scanning transmission electron microscopy showed nanometer-size WO_x clusters on SiO₂ and highly dispersed species on TiO₂. In situ XPS showed SiO₂-supported WO_x species reduce from an initial +6 oxidation state to primarily +5 after thermal treatment in H₂, while the fraction of +5 species detected on the P25-TiO₂ support did not change, regardless of reducing environment or addition of Pd.

Silica and titania-supported Pd-W catalysts were then evaluated for carboxylic acid reduction via the gas-phase conversion of propionic acid to propanal and propanol with H₂. High resolution STEM images confirmed the presence of nm-size Pd particles on both Pd-W-SiO₂ and Pd-W-P25-TiO₂ catalysts. During steady state conversion of propionic acid, the presence of Pd on both W-SiO₂ and W-P25-TiO₂ enhanced the selectivity and formation rate of propanal and propanol, with a combined selectivity of > 96 % at conversion levels of 1 % for Pd-W-SiO₂ and 9.2 % for Pd-W-P25-TiO₂. Over the P25-TiO₂-supported Pd-W catalyst, the reaction orders were 0.3 and zero in H₂ and propionic acid, respectively, while the apparent activation energy was 64 kJ·mol⁻¹. Although increasing the Pd loading on P25-TiO₂-supported W catalysts increased the combined propanal and propanol formation rate, the same effect had marginal influence on the formation rates over SiO₂-supported W catalysts. Most importantly, the P25-TiO₂ supported W catalysts exhibited order of magnitude higher formation rates of propanal and propanol compared to the SiO₂ analogs.

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Chapter 1: Introduction

1.1 Metal Oxides

Metal oxides are an important class of heterogeneous catalysts that are widely used for a variety of catalytic processes in the petrochemical, refining, and the conversion of biomass to specialty chemicals industries.^{1,2} Within these industries, they play a key role in reactions including, but not limited to, carbon-carbon (C-C) bond formation, transesterification of fatty acids, selective catalytic reduction and olefin metathesis.³⁻⁶ Their versatile use in numerous applications is due to their unique surface properties such as their acid-base nature and reduction-oxidation (redox) behavior.

The surfaces of metal oxides can vary chemically based on the identity of the ion and the surrounding environment. Metal cations can act as Lewis acid sites if they are able to accept lone pair of electrons while the adjacent oxygen anions act as the base sites. Additionally, if the cation possesses an -OH (hydroxyl) group, which can originate from H₂O dissociation, that hydroxyl group can behave as a Brønsted acid site by donating a proton.⁷ Cations that are not Lewis acidic can still form Lewis acid sites under certain conditions. For example, upon exposure to a reducing environment, cleavage of metal-oxygen bonds on the surface can occur, arising in oxygen vacancies thus exposing reduced cation sites, which can then act as Lewis acid sites. Moreover, if a promoter metal that is able to activate H₂ is in close proximity to a metal oxide, a reducing environment can also potentially allow for the formation of Brønsted acid sites on the oxide through the generation of hydroxyl groups via the spillover of atomic hydrogen from the metal onto the metal oxide.⁸⁻¹⁰ This concept will be discussed in greater detail in subsequent sections and

chapters, yet it helps demonstrate the variability of the metal oxide surfaces which can change depending on a variety of conditions.

Among the metal oxides, there are classes into which they can be generally grouped based on the aforementioned properties. Lewis acid metal oxides include but are not limited to Y_2O_3 , La_2O_3 , TiO_2 , ZrO_2 , and $Ta_2O_5^{11-13}$, while another class includes reducible metal oxides such as MnO_2 , TiO_2 , MoO_3 , WO_3 , and Re_2O_7 .¹⁴⁻¹⁶ Some also exhibit additional properties such as Brønsted acidity, as in the case of MoO_3 and WO_3 , or may be considered a more basic oxide such as Y_2O_3 and La_2O_3 .^{11, 13} There may also be overlap between the different classes. For example, La_2O_3 is considered a basic oxide while maintaining Lewis acidity, and WO_3 is considered a reducible oxide while known to exhibit Brønsted acidity. Furthermore, the ability to tune these acid-base and redox properties of metal oxides has been an ongoing research area over several decades. Efforts have included utilizing promoter ions as well as supports to alter the nature of the active site on the metal oxide surface.

Within the wide range of uses for metal oxides in heterogeneous catalysis, they are also extensively utilized as supports. Common supports include SiO₂, TiO₂, CeO₂, and Al₂O₃.^{1, 17-20} Silica, especially the mesoporous type, is widely used due to its relatively inert nature and high surface area,²⁰ while aluminosilicates such as crystalline microporous zeolites are popular supports in the petrochemical industry and in the field of biomass conversions.²¹ Both TiO₂ and CeO₂ are common among catalytic reactions requiring reduction and/or oxidation steps, such as those in automotive applications.^{3, 22, 23} Despite the pronounced use of supports with other active metal oxides and/or promotor ions as one catalytic system in contact with each other, the interactions between the different components are still actively studied.

1.2 Characterization of Metal Oxides

Understanding the chemical and physical nature of metal oxides is important and is studied through a variety of analytical and spectroscopic techniques. The techniques expanded upon here do not represent a comprehensive list of methods used in heterogeneous catalysis for the characterization of metal oxides nor all of the techniques used in the work presented in this dissertation. Instead, the ones elaborated on here are provided as an introduction for those more heavily discussed in the subsequent chapters.

1.2.1 X-ray Fluorescence Spectroscopy. X-ray fluorescence spectroscopy is a quantitative and qualitative technique widely used in heterogeneous catalysis for the analysis of material composition. Materials are irradiated with high energy X-rays which causes the ejection of electrons from atoms, also called ionization. Once electrons surpass their ionization energy, there is an instability due to the resulting holes from the ejected electrons as depicted in **Figure 1.1**. Electrons from an outer shell then drop into the resulting gaps through transitions occurring between the K, L, M, and N inner shells (orbitals). While many transitions can occur, typical transitions include K_a, which involves electrons from the L shell dropping to the K shell, K_β which involves an $M \rightarrow K$ transition, and L_a, which involves an $M \rightarrow L$ transition. These transitions then yield a subsequent release of energy in the form of a photon. This characteristic energy difference between the initial and final orbitals of the electron is then used to identify a particular atom while the intensity of the radiation is related to the quantitative analysis.



Figure 1.1: Representation of the working principle for XRF.

1.2.2 Diffuse Reflectance (DR) Ultra-violet (UV) Visible Spectroscopy. Ultra-violet visible spectroscopy is a useful technique used probe local environments of metal ions through the use of electronic and vibrational transitions in the wavelength region of 200-800 nm, with 200-400 nm considered the UV and 400-800 nm considered the visible region. Depending on the wavelength of light, atoms can absorb that light, which excites electrons from a ground state to an excited state. The measure of absorbance then provides detailed information regarding the coordination of metal centers, charge transfer transitions, cluster sizes and even semiconductor band gaps. Many heterogeneous catalysts are composed of powders that are in the range of micro to nanometer which is also on the same order of the wavelength of the light beam used during transmission UV-Vis.²⁴ As a consequence, the catalysts efficiently scatter the beam resulting in insufficient transmission. Due to this, UV-Vis characterization of heterogeneous catalysts relies on the principle of diffuse reflectance (DR) described by Kortum in 1969.²⁵ In short, the particles are irradiated with light that is either partially scattered or absorbed. An approximation is made in which no light is transmitted due to the thickness of the catalyst bed, i.e., an infinitely thick sample.

The scattered light is then collected by a detector and relates the detected light to the Kubelka-Munk (KM) function, **Eq 1.1**, which when plotted in a log function against the wavelength corresponds to the absorption spectrum typically provided by transmission UV-Vis spectroscopy. The relation between the light detected, scattering coefficient, *s*, and absorption coefficient, *k*, is provided in **Eq 1.1** where r_{∞} is the diffuse reflectance of light from an infinitely thick sample bed, i.e., the ratio of reflected light of the sample (R_{∞} sample), and a standard, (R_{∞} std). A variety of standards can be used depending on the necessary region and diffuse reflectance accessory. Friederike C. Jentoft summarizes many of these findings in her review.²⁶ In short, two of the most commonly used standards when characterizing supported metal oxides are high purity BaSO₄ and polytetrafluoroethylene (PTFE). Barium sulfate is an effective standard, reflecting >95% of the light within a range of 340-1400 nm, while PTFE is used down to 190 nm. Some groups have also used the background absorption of SiO₂ as the standard specifically for the characterization of SiO₂ supported metal oxides.^{26, 27}

$$f(r_{\infty}) = \frac{(1-r_{\infty})^2}{2r_{\infty}} = \frac{k}{s} \qquad \text{Eq 1.1}$$

Multiple features can arise within the plot relating the KM function to wavelength. These subsequent features can then be further used to determine the size of the oxide cluster size and provide information regarding the molecular structure. **Figure 1.2a**²⁸ shows a DR UV-Vis spectra of reference bulk tungsten oxide containing compounds. Based on transitions between ground and excited states, the features seen in the spectra of metal oxides are generally a result of ligand-to-metal-charge-transfers (LMCT) bands. Based on the known structure of compounds through additional techniques such as X-ray diffraction (XRD) and Raman spectroscopy, these LMCT bands can provide information regarding the nature of molecular structures present. For example, in the case of the reference tungsten oxide compounds in **Figure 1.2a**²⁸, LMCT bands in the range

of 218-223 nm correspond to isolated WO₄ units (these units do not represent the oxide stoichiometry, rather a molecular structure) such as the spectra of Na₂WO₄. Bands in the range of 250-270 nm correspond to distorted yet isolated WO₄ or WO₆ units, such as those in Al₂(WO₄)₃, while higher wavelength bands such as those of bulk tungsten trioxide, at 330 nm, correspond to infinite 3D tungsten oxide clusters. These absorption spectra can also be used to determine the band gap, which in turn helps determine the cluster size of the oxide. An example is shown in Figure $1.2b^{28}$ where the absorption spectrum is used to determine the bandgap (Eg) of selected tungsten oxide reference compounds via a Tauc plot²⁹, where the band gap of a semiconductor is plotted as a function of the KM function in the form of $(KM \cdot h\nu)^{1/\alpha}$, where h is Planck's constant, v is the photon's frequency, and a is a factor dependent on the electronic transition, such as direct or indirect, with values of 1/2 and 2, respectively.³⁰ A linear fit is then extrapolated to the intersection of the x-axis of the steep region to provide the estimated band gap. These band gaps can then be used in conjunction with the LMCT bands to determine the molecular structure of the metal oxide species present on the surface of the catalyst as well as the relative size of the oxide cluster, with higher bandgaps corresponding to a greater degree of isolation, i.e., a smaller cluster size.

The use of DR UV-Vis spectroscopy in heterogeneous catalysis is well known for both bulk and supported metal oxides.^{9, 27, 31-36} In fact, evaluations of bandgaps and LMCT bands are some of the most popular techniques used to investigate and provide information regarding the degree of isolation and molecular structures of supported metal oxides. However, there are limitations depending on the support and metal oxide used. For example, background absorption of a support, such as TiO₂ or Nb₂O₅, may prevent the use of this technique to accurately identify LMCT bands and quantify bandgaps for the metal oxide of interest.³⁷ While the use of electronic transitions in

optical spectroscopy to study metal oxides catalysts provides important information, it does not complete the picture of these complex materials, especially on an atomistic level.



Figure 1.2: (A) Diffuse Reflectance UV-Vis spectra of bulk tungstate reference compounds: (a) WO₃, (b) (NH₄)₆H₂W₁₂O₄₀, (c) Al₂(WO₄)₃, (d) Na₂W₂O₇, (e) Zr(WO₄)₂, (f) MgW₂O₇, and (g) Na₂WO₄. (B) Bandgap calculation based on DR UV-Vis spectra of select bulk tungstate reference compounds: (a) (NH₄)₆H₂W₁₂O₄₀, (b) Al₂(WO₄)₃, (c) Na₂WO₄. Reprinted with permission from *J. Phys. Chem. C*, **2007**, 111(41), 14933-15131. DOI: 10.1021/jp074219c Copyright 2007 American Chemical Society [28].

1.2.3 Microscopy. Microscopy (imaging) of heterogeneous catalysts has been utilized for decades to provide an accurate representation of the morphological and atomic environment of the catalyst surfaces. Transmission and scanning transmission electron microscopy (TEM and STEM, respectively) are two of the most widely utilized techniques for catalysts and reviews by Yang and co-workers, Zhou and co-workers, and Abhaya Datye summarize the use of these techniques in the scope of heterogeneous catalysis.³⁸⁻⁴⁰ In the same family of TEM and STEM, additional techniques have been developed such as bright-field (BF) TEM, annular dark field (ADF)-TEM and high angle annular dark-field (HAADF)-STEM. In the case of HAADF-STEM, the Rutherford scattered electrons provide the signals for the images. The electrons have a strong dependence on the atomic number (Z), typically in the order of Z^2 , and thus can provide micrographs of the area being imaged based on the Z-contrast. Additional techniques such as energy dispersive X-ray

spectroscopy (EDX) and electron energy loss spectroscopy (EELS) can also be used in conjunction with TEM and STEM to provide compositional information. The obvious advantage of these techniques is that they can provide identification of multiple surface species since many heterogeneous catalytic systems have been shown to contain different surface structures, such as dimers, and trimers on the same catalyst, as in the case of Pt supported on γ -Al₂O₃.⁴¹ However, microscopy does have limitations such as the difficulty in discerning species with similar atomic numbers due to the strong dependence of the Z-contrast, as in the case of Pd nanoparticles supported on CeO2.42 Another complexity arises due to the limited area imaged, which necessitates numerous images to provide evidence of homogeneity or heterogeneity of the catalyst surface. However, microscopy has been a beneficial technique in understanding the spatial distribution of atoms or species, especially in metal promoted metal oxide catalysts, such as Rh promoted WO_x catalysts as was shown by Ro and co-workers.⁴³ Moreover, the resolution of STEM microscopes is powerful enough to identify lattice spacing of crystal structures allowing for the determination of specific indices and planes of the species from metallic nanoparticles or metal oxides.⁴⁴ To this extent, it is highly utilized in the field of heterogeneous catalysis as it provides necessary insight into the speciation of both bulk and supported metal oxides.

1.2.4 Dihydrogen Temperature-Programmed Reduction. Temperature-programmed reduction is used as a descriptor for the oxidation-reduction properties of oxide materials including bulk and supported catalysts. A stream of reducing gas (typically H₂ or CO), diluted in a carrier gas (N₂ or He) is flowed over the sample while the temperature of the sample is ramped at a given rate (i.e., 1-20 K min⁻¹) in the range of 250 to 1300 K. The effluent gas concentration is monitored either by a thermal conductivity detector (TCD) or a mass spectrometer (MS). The changes in signal intensity across the temperature range provide information regarding the change in oxidation state

of the sample based on the uptake of hydrogen from the sample. Identification of the specific oxidation state can be done through either known reference compounds and/or the calculation of the hydrogen uptake per mol of metal based on the stoichiometry of the oxide. In general, H₂-TPR is very prevalent when studying interactions between metal promoted oxides as well as the interactions between the support and reducible metal oxides species. For example, many groups have used this technique to study the reducibility of a variety of oxides including tungsten, rhenium, and molybdenum as well as the effect of the support and even a PGM promoting the reduction of the oxide.^{43, 45-48} Through the use of H₂-TPR, it has been shown that the PGM can aid in lowering the initial reduction temperature of the reducible metal oxide, although this can be support dependent as well.^{46, 49} While this technique can provide information regarding the reduction profiles and even the provide the resulting oxide stoichiometry based on H_2 uptake, identification of oxidation states from the species of interest is not always straightforward and can become a challenge, especially when the support can play a role in the reducibility of the species or if there are mixed oxide species present.⁵⁰ Instead, additional techniques such as X-ray photo electron spectroscopy (XPS) are needed to effectively identify specific oxidation states.

1.2.5 X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy is a quantitative surface science characterization technique used to study the nature of the elements at or near the surface. Based on the work of Hertz's and Einstein's photoelectric effect, ^{51, 52} high energy photons, typically X-rays, irradiate the surface of a material causing the emission of electrons. The kinetic energy of the emitted electrons is then used to study the chemical state and electronic structure of the element. Eq 1.2 shows the photoelectric effect equation where E_B is the binding energy, hv is the photon energy of the X-ray source, E_K is the measured kinetic energy of the emitted electrons, and Φ is the work function term that is maintained constant and based on instrument calibration.

$$E_B = hv - E_K - \Phi \qquad \text{Eq 1.2}$$

Based on the given values, the resulting equation provides the binding energy which is the energy required to remove an electron from its given shell. These energies are characteristic for each element and each particular electron shell and thus become descriptors for the electronic environment of the given atom. Based on the electronegativity of surrounding atoms, the binding energy of an electron in a specific atom can change. For example, oxygen is more electronegative than carbon, thus a C-O bond would induce a higher binding energy of electrons relative to those in a C-C bond. Based on such effects, XPS is widely used to determine the oxidation state and can also help understand the local environment of a specific atom.

A typical photoemission spectrum can have multiple components depending on the element, region, and oxidation states present. Fitting of peaks is generally necessitated depending on the region of interest due to the complex nature of the features present. The regions are based on the element as well as the orbital shell being scanned, i.e., the s, p, d, and f. All of the orbitals, apart from the s, for any given element produce two features for each species also referred to as doublets. These doublets arise from the spin-orbit splitting (aka coupling) and are denoted based on their angular quantum number, l (0,1,2,3) and a spin number s (±1/2), in the form of their total angular momentum quantum number j, as the subscript, where j = l + s. For example, the tungsten 4f region consists of a W 4f_{7/2} and W 4f_{5/2} doublet. The relative intensities of the doublets are based on the degeneracy of the states and are calculated by 2j + l. Thus, the intensity ratio of the W 4f_{7/2} and W 4f_{5/2} doublet would be 4:3 and this ratio is subsequently used as a fitting parameter for the peak areas. This ratio is used as a fitting parameter for most p, d, and f orbitals features, unless the doublets have a separation that is below a reasonable resolution to accurately fit, in which case fitting is done to only one peak and the area ratio is disregarded.⁵³ Additional fitting parameters

can also be used, such as the binding energy difference between the doublets in the p, d, and f regions for each given species, the full-width-half-maximum (FWHM) of each separate peak, and the corresponding binding energy difference between different species. Practical guides on accurate peak fitting can be found throughout literature.⁵⁴ Most of these peak fitting parameters and values are generally well-established in literature and can be found for most elements and their known oxides.⁵⁵ **Figure 1.3** shows an example photoemission spectrum along with subsequent fitting parameters for a bulk WO₃ sample.⁵⁵ The main features that are evident are the W 4f_{7/2} and 4f_{5/2}, peaks B and E respectively, of the WO₃ species representing the +6 oxidation state for W. The peak at the lower binding energy, peak A, corresponds to the W 4f_{7/2} of WO₂, which is in a +4 oxidation state and its W 4f_{5/2} feature, peak C, which has a binding energy difference of 2.1 eV

just as the features for the +6 species.

Sample Description: WO3 (99.995%) Aldrich Lot# 00107KM JV, 3mm pellet, screen, 90 TOA Counts



Figure 1.3: Photoemission spectrum of the W 4f region for WO₃ with subsequent fitting parameters. Reprinted with permission from Crist, V. B. *Handbooks of Monochromatic XPS Spectra: Volume 2: Commercially Commercially Pure Binary Oxides*; XPS International LLC, 2019. Copyright 2019 XPS International, LLC [55].

Photoemission spectra are generally collected under near vacuum conditions; thus, typical XPS applications in the field of catalysis include the study of catalyst surfaces prior to and after reaction or after in situ pretreatment conditions instead of operando. Interestingly, the use of XPS at elevated pressures has been around for a few decades in the form of near-ambient-pressure XPS, AP-XPS,⁵⁶ but this technique is not utilized in this work. As with all characterization techniques, there are limitations for the use of XPS based on experimental setup, instrument limitations, elements used, and peak fitting parameters. In XPS, the accuracy of determined chemical states based on binding energy heavily relies on a calibration of said binding energy scale. One common example is use of the C 1s peak, often referred to as the adventitious carbon, described as a thin layer of carbon present on the surface of materials that are exposed to air.⁵⁷ Furthermore, the exact value of this peak differs throughout literature, typically in the range of 284 eV to 285 eV and the use of the peak as a reliable reference has long been debated.^{58, 59} This thin layer of carbonaceous material can also disappear if a sample is annealed at an elevated temperature, thus making the reference of binding energies difficult.⁶⁰ Depending on the elemental composition of the sample, other binding energy references can be used, such as a single Si 2p peak of the support (resolution of spectra may prevent from accurate detection of the 2p doublet, i.e., 2p_{3/2} and 2p_{1/2}), although consideration should be taken to ensure the reference binding energy corresponds to the known species present on the surface, i.e., SiO₂.⁵⁵ Additionally, certain regions of different elements overlap, such as the Ti 3p and W 4f regions, thus peak fitting can become complex due to the nature of the different features, especially when multiple species are present. To ensure an additional level of reliability, spectra of additional regions of the same element are also collected to be used in peak fitting, like in the case of the Ti 2p and Ti 3p regions. However, intensity of certain elemental regions may not always provide the needed level of accuracy for reliable peak

fitting.⁵⁴ While the limitations and disadvantages discussed here are well documented for XPS, it is a generally popular technique in the heterogeneous catalysis field, among many others. As such, the use of certain parameters regarding peak fitting or binding energy referencing are well documented and can be accurately evaluated throughout the literature.

All of the techniques discussed here provide important information regarding the molecular structures, local atomic environment, and speciation of metal oxide catalysts. Additional techniques such as Raman spectroscopy, infrared (IR) spectroscopy, XRD, N₂-physisorption, H₂-chemisorption and X-ray absorption spectroscopy (XAS) are also widely used in conjunction with those outlined here.^{22, 27, 46, 61 34, 62} Generally, a combination of these techniques is used to better understand the nature of the catalytically active metal oxide species as well as their interactions with supports and/or promoter ions.

1.3 Supported Metal Oxides in Heterogeneous Catalysis

Supported metal oxides are widely used in a variety of catalytic reactions that involve the conversion of oxygenated molecules, both industrially and at the fundamental research level.^{2, 18} Based on some of their unique properties such as their acid-base nature and reducibility, the choice of a specific metal oxide can vary even during the same reaction. For example, in the case of the conversion of ethanol to 1,3-butadiene (ETB) as shown in **Figure 1.4** which follows the generally accepted Toussaint-Kagan mechanism⁶³, where ethanol is converted to acetaldehyde which is followed by a C-C coupling step to form crotonaldehyde with a subsequent hydrogenation to form crotyl alcohol and a final dehydration step to form 1,3-butadiene (butadiene), the metal oxide component of the catalyst (ETB catalysts typically consist of a noble metal such as Ag, metal oxide, and support) is known to be responsible for the C-C bond formation step. This is due to

their Lewis acid-base sites, with the cation acting as the Lewis acid and adjacent oxygen as the base.⁴ As such, past and current research has focused on numerous supported metal oxides which include SiO₂ supported ZrO₂, Nb₂O₅, TiO₂, Al₂O₃, Y₂O₃, and Ta₂O₅.^{4, 12, 64, 65} All are able to catalyze C-C bond formation leading to the production of butadiene, however selectivity to butadiene has been shown to vary depending on the identity of the Lewis acid cation. For example, Sushkevich and co-workers showed a selectivity range of 40 to 74 %, between SiO₂ supported TiO₂ and ZrO₂, respectively (both catalysts were also promoted with Ag as the noble metal).⁶⁴ Additionally, the product distribution to butanol, a base catalyzed side product from the same reaction mechanism⁶⁶ as shown in **Figure 1.4** and higher chain coupling products, which stem from subsequent C-C coupling and hydrogenation steps has also been shown to depend on the identity of the metal oxide, with oxides regarded as more basic such as Y₂O₃ and La₂O₃ showing a higher distribution to butanol and higher chain coupling products compared to more acidic oxides.^{67, 68}



Figure 1.4: Toussaint-Kagan mechanism [63] for the conversion of ethanol to butadiene via the Lebedev process, as well as the additional pathway for butanol, via the Guerbet reaction.

Efforts have been made to alter the acid-base characteristics and the molecular structure of the active metal oxide by using different supports. One of the most promising effects has been shown with the use of Beta zeolite as the support, specifically de-aluminated Beta zeolite. Groups have shown zeolite supported tantalum, yttrium, and lanthanum oxides to have conversion, selectivity, and/or rates for the conversion of ethanol to butadiene and higher chain C₄₊ products compared to

their SiO₂ supported analogs.^{67, 69, 70} Arguments have been made as to the reason for the higher activity, with a variety of characterization techniques supporting each. These explanations range from the confinement effect of the zeolite micropores to the ability of the zeolite to alter the structural environment around the Lewis acid cationic active site. Regardless, the interaction between the support and the active metal oxide species is highly prominent and remains a fundamental interest, especially in the conversion of ethanol to higher value products such as butadiene.

Lewis acidic metal oxides that have appropriate active sites for the C-C bond formation step necessary in the ETB reaction are often limited in the scope of modifications such as reducibility and/or ability to catalyze Brønsted acid site reactions such as the reduction of carboxylic acids into their corresponding aldehydes and alcohols.^{46, 49, 71, 72} When promoted with a platinum group metal (PGM), reducible metal oxides such as TiO₂, Re₂O₇, MoO₃, and WO₃ have been shown to be active catalysts for this reaction.^{46, 49, 61, 71-74} For example, SiO₂ supported Pd-Re and Pd-W (both Re and W are in oxide form, i.e., ReO_x and WO_x, where x is used for oxide stoichiometry due to the reducible nature of the oxide species) have both been tested in the conversion of propionic acid to propanol with propanal (propionaldehyde) as the intermediate as shown in Figure 1.5, and have showed a selectivity of >80% to propanol.^{46, 71} Likewise, Pt-TiO₂ catalysts have been tested in the conversion of steric acid and showed a 90% selectivity to stearyl alcohol.⁷³ While TiO₂ by itself can be an active oxide, it is also widely used as a support, as in the case of Pt-Re-TiO₂ and Pd-W-TiO₂ catalysts, both of which have shown high activity in the conversion of carboxylic acids.^{71,74} There is still an ongoing discussion on the effect of the reducible metal oxide identify as well as the effect of support. However, the use of the PGM, as a promoter, further adds complication in the study of these reducible metal oxides.



Figure 1.5: Reaction pathway for the conversion of propionic acid to propanal and subsequently propanol.

Metals such as Pd and Pt are known to aid in the dissociation of H_2 .⁷⁵ While this dissociation allows for atomic hydrogen to participate in the reaction mechanism, when the metal oxide is in close contact with the Pt group metal, spillover of atomic hydrogen has also been shown to further promote the reduction of the metal oxide species, as seen in **Figure 1.6**⁷⁶. This interfacial phenomenon was first noticed by Khoobiar, who reported the reduction of WO₃ to WO_{3-x} by H₂ when in physical contact with Pt/Al₂O₃,⁷⁷ after which Boudart *et al.* described it as the migration of H atoms between the metal and support as "spillover" over a Pt-WO₃ catalyst.⁷⁸



Figure 1.6: Artistic representation of atomic hydrogen spilling over from a Pd nanoparticle (navy blue) onto ReO_x (red and light blue) species during the reduction of carboxylic acid to an aldehyde intermediate and alcohol product. Reprinted with permission from *AIChE Journal*, **2018**, *64* (11), 3778-3785. DOI: 10.1002/aic.16385. Copyright 2018 American Institute of Chemical Engineers [76]

While spillover is referred to as the transfer of species from one surface to another, spillover of hydrogen is the most commonly studied type, with a review by Prins summarizing this effect in a range of reducible supports and oxides, including TiO₂, MoO₃, and WO₃.⁷⁵ The effect of hydrogen spillover for these PGM-promoted reducible metal oxides has been shown to affect the molecular structure of the active oxide species in numerous instances.^{8, 49, 79, 80} In one example, hydrogen spillover from Pt to WO_x species on a Pt-W-TiO₂ catalyst has been shown to reduce the W=O functional group, via Raman spectroscopy, thereby increasing the W(V)/W(VI) ratio and generating in situ Brønsted acid sites.¹⁰ As Brønsted acid sites have been hypothesized to play a key role in the reduction of carboxylic acid to their corresponding aldehydes and alcohols, the spillover effect may contribute to the generation of active sites for this process.⁴⁶ Overall, the interactions between the support, promoter ions, and the active metal oxides have been of fundamental interest in heterogeneous catalysis, especially in the conversion of oxygenates to higher value products. As described, the identity of metal oxide, support, and even the promoter metal can alter catalytic activity due to a variety of factors. None the less, the effect these interactions have on the catalytic performance can be better understood when the reactivity is coupled with various characterization techniques.

1.4 Objectives of this Dissertation

The correlation of acid-base nature and reducibility to the functionality of supported metal oxides in a plethora of catalytic applications has been consistently studied over the past several decades. This dissertation aims at expanding this field by studying an array of supported metal oxides for the conversion of oxygenates. In Chapter 2 of this dissertation, the aim is to directly compare the oxides of four Lewis acid cations (Ta, Y, Pr, and La) supported on SiO₂ or Beta zeolite for the conversion of ethanol to butadiene by a catalyst system comprising of a physical mixture of Ag-SiO₂ and a separate M-SiO₂ or M-HBZ (M = Ta, Y, Pr, and La) component. Diffuse-reflectance UV-vis spectroscopy and XPS provided insights into the supported metal oxide cluster size, and the oxidation state of the supported Lewis acid cations, respectively. The acid-base nature and functionality correlation of the supported catalysts in the ETB reaction utilized 2-propanol decomposition to propene and acetone as a probe reaction for acid strength.

In Chapters 3 and 4 of this dissertation, the focus is shifted on Pd promoted tungsten oxide catalysts for the conversion of propionic acid to propanol. The effect of support, cluster size, and the influence of hydrogen spillover on the reduction of SiO₂ and TiO₂ supported Pd-W catalysts is studied with a variety of characterization techniques including H₂-TPR, DR UV Vis spectroscopy and HAADF-STEM imaging. Quantum chemical calculations performed by Anukriti Shrestha were used together with experimental observations to describe the speciation of supported WO_x species. The distribution of tungsten oxidation states formed from various thermal treatments was quantified by in situ XPS and XAS. Finally, the reactivity of SiO₂ and TiO₂-supported Pd-W catalysts was investigated over steady-state reduction of propionic acid to propanal and propanol.

The objectives of this dissertation are:

- To understand the effect of different Lewis Acid cations (Ta, Y, Pr, and La) and support structure (amorphous SiO₂ or crystalline Beta zeolite) for the conversion of ethanol to butadiene by a catalyst system comprising of a physical mixture of Ag-SiO₂ and a separate M-SiO₂ or M-HBZ (M= Ta, Y, Pr, and La) component.
- To determine the influence of hydrogen spillover, support (insulating vs. reducible) and cluster size on the reducibility of SiO₂ and TiO₂-supported tungsten oxides when promoted with palladium nanoparticles.
- 3. To expand on the effect of support for SiO₂ and TiO₂-supported Pd-W catalysts for the reduction of propionic acid to propanal and propanol.

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Chapter 2: Cascade Reaction of Ethanol to Butadiene over Ag-Promoted, Silica or Zeolite Supported Ta, Y, Pr, or La Oxide Catalysts

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Abstract

Ethanol converts to 1,3-butadiene in the presence of suitable multifunctional catalysts. In this work, Lewis acid cations Ta, Y, Pr, and La were dispersed on amorphous silica or beta zeolite, and after physically mixing with silica-supported Ag nanoparticles, were tested in the cascade reaction of ethanol to butadiene at 573 K. The Lewis acid catalysts were characterized by X-ray fluorescence, N₂ physisorption, scanning transmission electron microscopy (STEM), X-ray diffraction, diffuse reflectance (DR) UV-Vis and X-ray photoelectron spectroscopy. Highresolution STEM images confirmed the small oxide cluster size on the silica support. Results from DR UV-Vis spectroscopy showed zeolite-supported Ta and Pr catalysts had a smaller metal oxide cluster size, relative to their SiO₂ counterparts. X-ray photoelectron spectroscopy confirmed the oxidation state of the cations supported on the zeolite remained the same as that of their SiO₂supported analogues. The selectivity of the C4 coupling products toward butadiene relative to butanol correlated with acid strength of the Lewis acid cations, as evaluated by the 2-propanol decomposition reaction to propene and acetone, with Ta being the most selective. The rate of C-C coupling over the zeolite-supported cations was enhanced by an order of magnitude compared to those cations supported on amorphous SiO₂.

2.1 Introduction

Butadiene (1,3-butadiene; 1,3-BD) is an important molecule derived from fossil resources that is utilized as an intermediate in the production of various polymers and synthetic rubbers such as nitrile-butadiene and styrene-butadiene rubbers (NBR, SBR).^[1-3] Butadiene is a byproduct of the naphtha steam cracking process used to produce ethylene. Since 2010, an inexpensive supply of shale-derived natural gas in the United States has triggered shift in steam cracking feedstock for ethylene production from naphtha to ethane. This change to ethane feedstock in steam cracking results in a considerably lower yield of butadiene byproduct relative to the naphtha feedstock process.^[1, 2] Over the same timeframe, bioethanol has seen a production increase and an average price decrease.^[4] Thus, there is renewed scientific and industrial interest in the catalytic conversion of ethanol to butadiene, either by the Lebedev process, which uses a single ethanol feed, or the Ostromislensky processes, which utilizes a feed mixture of ethanol and acetaldehyde.^[2, 4]

Previous comparisons of the two catalytic processes have shown that the Lebedev process has a marginally smaller carbon footprint than naphtha cracking and is less environmentally damaging than the Ostromislensky process.^[4] Since the Ostromislensky process also requires additional resources and infrastructure to produce a separate feed stream of acetaldehyde to react with ethanol, the Lebedev process is the preferred catalytic method. The Lebedev process is very similar to the Ostromislensky process where the acetaldehyde is produced in situ in the cascade reaction of ethanol. The conversion of ethanol to butadiene has been widely studied and is generally believed to follow the Toussaint-Kagan reaction network shown in **Figure 2.1**.^[5] In this network, ethanol is first dehydrogenated to acetaldehyde. Both the Lebedev and Ostromislensky processes then follow the same reaction path after ethanol dehydrogenation in which acetaldehyde undergoes aldol condensation (forming a C-C bond) to produce crotonaldehyde. Hydrogenation of

crotonaldehyde to form crotyl alcohol is proposed to occur by a Meerwein-Ponndorf-Verley (MPV) reduction with ethanol.^[1, 2] Crotyl alcohol subsequently dehydrates to form butadiene or hydrogenates to form butanol, a commonly observed side product.^[1, 2, 6] Butanol is considered the main product in the Guerbet reaction, which follows a similar reaction network utilizing ethanol as the feedstock over a less acidic catalyst such as hydroxyapatite.^[6] Undesired ethylene and diethyl ether form via ethanol dehydration on acid sites of the catalyst.



Figure 2.1: Toussaint-Kagan reaction network for the Lebedev process for converting ethanol to butadiene, butanol, and undesired acid-catalyzed byproducts.

Catalytic conversion of ethanol to butadiene via the Lebedev process commonly utilizes three components, namely metal nanoparticles, transition metal oxides, and supports. Metals such as Ag and Cu are active in ethanol dehydrogenation to acetaldehyde, while supported oxides of Zr, Y, and Ta are effective in the coupling steps necessary for C4 formation (butadiene or butanol).^[7-10] Butanol may also potentially form via hydrogen transfer to crotonaldehyde to form butyraldehyde and subsequent hydrogenation to butanol. Nevertheless, the Lewis acid-base sites of the transition metal oxides are claimed to be the active sites for aldol condensation and hydrogen transfer steps in the Toussaint-Kagan reaction network.^[9, 11-13]

The performance of different Lewis-acid cations in the conversion of ethanol (Lebedev) or an ethanol-acetaldehyde mixture (Ostromislensky) to higher value C4 or C4+ products such as

butadiene and butanol has been described in previous studies. For example, Toussaint and Dunn first patented Ta-SiO₂ as an effective catalyst for the conversion of an ethanol-acetaldehyde mixture to butadiene in 1947.^[14] Corson et al. later reported a butadiene yield of 69% (2.75 mole ratio of ethanol : acetaldehyde) over their Ta-SiO₂ catalyst.^[15] More recently, Zhu et al. reported a selectivity to butadiene and butanol of 93% (82 % butadiene and 11% butanol) over Y-SiO₂ at an ethanol/acetaldehyde conversion of 31% (75:25 wt% of ethanol : acetaldehyde).^[10] Of the Lebedev catalysts, Sushkevich et al. demonstrated a butadiene selectivity of 74% over their Ag-promoted Zr-SiO₂ catalyst at an ethanol conversion of 30%.^[9] Additional information from prior studies can be found in recent reviews of the catalytic conversion of ethanol to butadiene.^[1, 2]

The observations reported in the literature can be broadly explained according to the acid-base character of the transition metal oxides, which depend on cation size, cation charge, and oxide surface structure. For example, in Period 6 of the Periodic Table, the oxide surface of Ta(V) is a stronger Lewis acid compared to Pr(III), which is a stronger Lewis acid relative to La(III). Moreover, appropriate strength Lewis acid components are necessary in a selective catalyst to produce butadiene from ethanol while simultaneously avoiding the formation of undesired ethanol dehydration side products.

Recently, the design of an effective ethanol-to-butadiene catalyst has included crystalline beta zeolite as an alternative support to amorphous SiO₂. Dai et al. showed a Zn-Y-Beta catalyst to have a butadiene selectivity of 63% at an ethanol conversion of 82 % while also showing the butadiene productivity $(g_{BD} \cdot (g_{cat})^{-1} \cdot h^{-1})$ to be five times higher than that of Zn-Y-SiO₂.^[16] Qi et al. reported an order of magnitude increase in specific rate of butadiene formation from ethanol and acetaldehyde when Y was supported on beta zeolite compared to silica.^[17] Furthermore, Zhang et al. also reported an initial rate of C-C coupling over Cu-Zn-Y-Beta catalysts that was more than 9

times higher compared to a SiO₂ supported catalyst during butene rich C3+ production from an ethanol and acetaldehyde feed (0.8 kPa acetaldehyde, 7.9 kPa ethanol, balance with H₂).^[18] Cordon et al. followed up with a study of a Cu-La-Beta catalyst that showed a high C4+ olefin selectivity of 73% at an ethanol conversion of 98%.^[19] Similarly, Kyriienko et al. showed that a Cu-Ta-Beta catalyst was able to achieve 73% selectivity to butadiene at an ethanol conversion of 88%.^[20] Regardless of the identity of Lewis acid cation (Y, La, or Ta) and the support (amorphous SiO₂ or crystalline beta zeolite), there is strong agreement that the transition metal cation is the active site for the C-C coupling step in the conversion of ethanol to butadiene and other high value C4 and C4+ products. The reason for the substantial reported increase in rate associated with zeolite support remains unclear.

Direct comparisons among Lewis acid cations and supports used in the valorization of ethanol to C4 and C4+ products has been limited because the co-impregnation of components such as Zn and/or Cu have been previously shown to exhibit Lewis acid character of their own when supported on beta zeolite.^[18] Previously, our group has shown that a co-impregnated Ag-ZrO_x-SiO₂ catalyst behaves similarly to that of a catalyst system comprised of a physical mixture of Ag-SiO₂ and ZrO_x-SiO₂.^[13] The physical separation of Ag metal and ZrO_x on different support particles allowed for a direct evaluation of performance of the different components without mutual interference. In the current work, we used the same strategy to explore the influence of different transition metal cations as well as different support structures at the same reaction conditions without the interference of Ag.

This works aims to directly compare four Lewis acid cations (Ta, Y, Pr, and La) supported on SiO₂ or beta zeolite (HBZ) in the conversion of ethanol to butadiene by a catalyst system comprised of a physical mixture of Ag-SiO₂ and a separate M-SiO₂ or M-HBZ (M= Ta, Y, Pr, and La)

component. Diffuse-reflectance (DR) UV-vis spectroscopy and X-ray photoelectron spectroscopy (XPS) provided insights into the supported metal oxide cluster size and the oxidation state of the supported Lewis acid cations, respectively. The performance of the supported catalysts in the cascade reaction of ethanol was correlated to the rate and selectivity of 2-propanol decomposition to propene and acetone.

2.2 Materials and Methods

2.2.1 Catalyst Synthesis. High-purity SiO₂ (Sigma-Aldrich, Davisil 635, 60 Å, 480 m² ·g⁻¹, 150-250 µm) was used as the support for silver and M(Ta, Y, Pr, and La)-SiO₂ systems. Catalysts were synthesized by the incipient wetness impregnation (IWI) method. Briefly, the desired amount of precursor was mixed with an amount of solvent, either with distilled, deionized (DI) water or anhydrous ethyl alcohol (Sigma-Aldrich, \geq 99.5%), to achieve a solution that was equal to the pore volume of the support. This solution was added drop-wise onto the support until the point of incipient wetness. The mixture was then left to dry overnight at 293 K in ambient air, followed by a secondary drying for 2 h at 393 K, and then thermally treated under 100 cm³ ·min⁻¹ flowing medical air (Praxair) with time and temperature depending on the composition as shown in **Table A1**. The catalytic systems are referred to by their nominal compositions.

Beta Zeolite (ACS Material, 0.55-0.70nm pore, MR 40, SiO₂:Al₂O₃ molar ratio = 40) was used as the support for M(Ta, Y, Pr, and La)-HBZ systems. The X-ray fluorescence (XRF) analysis of the parent zeolite showed an Al content of 2 wt%. Beta zeolite was dealuminated in 13M HNO₃ at 373 K for 20 h, washed to a pH of 6-7, and dried at 393 K overnight. The dealuminated H beta zeolite is referred to as DeAl-HBZ. Results from XRF revealed an Al content of 0.2 wt% following the dealumination process. Zeolite-supported catalysts were synthesized using a wetness impregnation method previously described by Qi et al.^[17] A solution of precursor and solvent was added to the HBZ support to achieve a slurry of HBZ. The slurry was dried at room temperature for 5 h followed by an overnight drying at 393 K after which the powder was ground for 20 min. The resulting powder was thermally treated at the same conditions as their SiO₂ supported analogues mentioned above and reported in **Table A1**.

Reference bulk oxides were used as received from each supplier. Compounds include Ta_2O_5 (Aldrich, 99.99%), Y_2O_3 (Aldrich, 99.99%), Pr_2O_3 (Sigma-Aldrich, 99.9%), and La_2O_3 (Sigma-Aldrich, \geq 99.9%).

2.2.2 Catalyst Characterization. X-ray fluorescence measurements were performed by Horiba Scientific (Piscataway, NJ) with an XGT-9000 XRF analytical microscope, equipped with a 50W Rh anode X-ray tube. Spectra were collected in partial vacuum over an area of 12.5 mm^2 , an energy resolution of less than 143 eV at Mn-K α , and an accelerated voltage of 50 keV. Component concentrations were calculated using the Fundamental Parameters Method.

Surface areas were obtained by physisorption of N_2 (Praxair, 99.999%) at 77 K with a Micromeritics ASAP 2020 Plus instrument utilizing the BET method. Sample sizes of 150-300 mg were used for analysis. Prior to analysis, each sample was evacuated at 723 K under vacuum. Pore volumes of the zeolite samples were determined from the N_2 uptakes measured at a relative pressure (P/P_o) of 0.3.

X-ray diffraction (XRD) patterns were obtained on a PANalytical Empyrean diffractometer using Cu-K α radiation (λ of 1.54Å) generated at 45 kV with a 40mA incident X-ray source. Scans were collected in the range of $2\theta = 15-80^{\circ}$ with a 0.015° step size.

High resolution high-angle annular dark field (HAADF) scanning transmission electron microscope (STEM) images were recorded on a Thermo Fisher Scientific Themis Titan 3591

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scanning transmission electron microscope operating at 200 kV and equipped with a monochromator and probe correction. The STEM-HAADF detector (Fischione) collection angle was set to 50-200 mrad at 115 mm camera length. Samples were slurried in ethanol and deposited on lacey or holey carbon films supported on copper grids.

Diffuse reflectance ultraviolet-visible spectra were collected on a PerkinElmer Lambda 850+ UV Vis spectrometer with a Harrick Praying Mantis Diffuse Reflectance Accessory. Polytetrafluoroethylene (Sigma-Aldrich, powder, >40 μ m) used as the reflectance standard with spectra recorded from 190 to 600 nm. In one case, a Harrick reactor cell was utilized for pretreatment of the sample in inert atmosphere at 773 K, where He (99.999%, Praxiar) was passed through an OMI purifier (Supelco) at 70 cm³ ·min⁻¹ prior to admission to the cell.

X-ray photoelectron spectroscopy measurements were performed using a PHI VersaProbe III spectrometer equipped with a monochromatic Al k-alpha X-rays (1486.6 eV) and a hemispherical analyzer. A 1000 µm sample spot size was utilized with a pass energy of 55 eV and an X-ray beam size of 100 µm for high resolution region scans. An internal electron flood gun (1 ev) and/or low energy Ar ion gun were utilized during data collection as neutralization systems. Binding energies for all elements were referenced to the Si 2p peak at 103.5 eV.^[21] Peak fitting was performed on the high-resolution scans using a Gauss-Lorentz fit (90% Gauss) with a Shirley background. Peak area ratios between doublets (i.e 7/2 and 5/2, 5/2 and 3/2, or 3/2 and 1/2) were held constant while fits were made to minimize chi squared values.

2.2.3 Catalytic Reactions of Ethanol and 2-Propanol. The cascade reaction of ethanol to butadiene and other products was carried out at 1 atm in a continuous downflow fixed bed titanium reactor tube with an internal diameter of 0.7 cm and outer diameter of 1 cm. A layer of quartz wool (1 cm in height) was placed in the reactor to hold the catalyst in place. Reaction temperature was

measured by a thermocouple inserted at the top of the reactor and controlled by a temperature controller (Omega). Fiberglass heating tape was wrapped around the reactor to minimize temperature gradients. Catalysts were pre-treated in-situ at 623 K for 1 h in 30 cm³ ·min⁻¹ flowing H₂ (Praxair, 99.999%).

Liquid ethanol (Koptec) was fed to a vaporizer via a syringe pump (ISCO). Carrier gas N_2 (Praxair, NI 5.0 UH-T, 99.999%) was mixed with the ethanol in the vaporizer to give a gas composition of 94 mol% N_2 and 6 mol% ethanol, which was subsequently fed to the reactor. Reaction temperature was maintained at 573 K.

Decomposition of 2-propanol was performed with the same reactor setup described above. Liquid 2-propanol (Sigma Aldrich, \geq 99.5%) was fed to a vaporizer via a syringe pump (ISCO). Afterward, the carrier gas N₂ (Praxair, 99.999%) was mixed with the 2-propanol in the vaporizer prior to the reactor either at 97 mol% N₂ and 3 mol% 2-propanol or 78 mol% N₂ and 22 mol% 2-propanol, depending on the catalyst. Reaction temperature was varied between 473 and 523 K.

Reaction products were analyzed by a Shimadzu GC-2014 AT equipped with a Shimadzu MS-5A capillary column and a flame ionization detector. Methane (Praxair, 99.97%) was added downstream of the reactor prior to entering the GC and was used as an internal standard for quantification.

Conversion and product selectivity were calculated on a carbon atom basis, defined in Eq 2.1 and Eq 2.2, respectively, where M_0 is the inlet molar flow rate of ethanol, M_i is the molar flow rate of product *i*, and n_i is the number of carbon atoms in product *i*. The apparent site time yield of a specific product (STY) was calculated using Eq 2.3, where M_m is the moles of Lewis acid cation in reactor, determined from catalyst mass and XRF analysis, which assumes all cationic sites are

accessible and are the only sites involved in the catalysis. Thus, the STY was used only to compare reactions that occur on the metal cations, such as C-C coupling and 2-propanol decomposition.

Products presented in tables and figures are C₂H₄ (ethylene), (C₂H₅)₂O (diethyl ether), C₂H₄O (acetaldehyde), C₄H₆ (1,3-butadiene), and C₄H₉OH (butanol) for the ethanol cascade reaction and C₃H₆ (propylene), C₃H₆O (acetone) and (C₃H₇)₂O (diisopropyl ether) for the 2-propanol decomposition reaction. Unidentified components in the "others" column for the ethanol cascade reaction include ethane, propylene, butenes, acetone, crotonaldehyde, butyraldehyde, and C₄₊ hydrocarbon by-products. The mass ratio of Ag-SiO₂ to M-SiO₂ or Ag-SiO₂ to M-HBZ in the reactor was kept constant at 1:4 for M-SiO₂ and 1:0.5 for M-HBZ. For example, 0.1 g of Ag-SiO₂ was physically mixed with 0.4 g of 2Y-SiO₂ while an analogous HBZ –based catalyst utilized a physical mixture of 0.1 g of Ag-SiO₂ to M-SiO₂ was chosen to be 1:4, however, this ratio was adjusted for M-HBZ samples as their relative activity was an order of magnitude greater than that of their silica analogues.

$$conversion (C\%) = 100 \% \cdot \left(\frac{\sum n_i M_i}{2M_0}\right) \qquad \text{Eq 2.1}$$

$$selectivity_i (C\%) = 100 \% \cdot \left(\frac{n_i M_i}{\sum n_i M_i}\right) \qquad \text{Eq 2.2}$$

$$STY_i = \left(\frac{M_i}{M_m}\right)$$
 Eq 2.3

2.3 Results

2.3.1 X-ray Fluorescence, Nitrogen Physisorption, and Microscopy. Results from elemental analysis and N₂ adsorption on the catalysts are summarized in **Table 2.1.** The samples are denoted by their nominal cation loading with XRF analysis showing the measured weight percent. The

samples containing transition metal cations on SiO₂ retained the high surface area of the support, Davisil 635 SiO₂, as revealed by the BET surface areas in **Table 2.1**. The dealumination process used in this work successfully lowered the Al content of HBZ by an order of magnitude (from 2 wt% to 0.2 wt%) without destroying the pore volume of the parent zeolite. The X-ray diffraction patterns of HBZ, DeAl-HBZ, and 2Y-DeAl-HBZ (**Figure A1**) as well as similar pore volumes across the series of zeolite samples suggest the zeolite structure also remained intact after cation incorporation.

Table 2.1. Elemental analysis and textural properties of Elewis acid catalysis							
Sample	XRF Composition - (wt% Cation)	N ₂ Physisorption					
		BET Surface Area	Pore Volume ^a				
		$(m^2 \cdot g^{-1})$	$(cm^{3} \cdot g^{-1})$				
SiO ₂		480	0.80				
H-Beta Zeolite			0.27				
(HBZ)		-	0.27				
DeAl-HBZ		-	0.27				
10Ta-SiO ₂	8.0	511	0.90				
4Ta-SiO ₂	3.4	493	0.87				
2Ta-SiO ₂	1.2	469	0.92				
2Ta-HBZ	1.7	-	0.27				
4Y-SiO ₂	2.9	458	0.83				
$2Y-SiO_2$	1.3	476	0.86				
2Y-HBZ	1.2	-	0.27				
4Pr-SiO ₂	4.6	468	0.94				
4Pr-HBZ	3.9	-	0.27				
4La-SiO ₂	3.4	447	0.82				
4La-HBZ	4.4	-	0.27				

Table 2.1: Elemental analysis and textural properties of Lewis acid catalysts

 a BJH desorption cumulative volume of pores for SiO₂ catalysts, and calculated at P/P_o = 0.3 for HBZ catalysts.

High resolution HAADF STEM images of SiO₂-supported Ta were obtained to provide an estimate of metal oxide cluster size and are shown in **Figure 2.2**. The image in **Figure 2.2b** shows metal oxide domains of about 1 to 2 nm in size. Moreover, the contrast differences with the support associated with the clusters suggest that many may be raft-like instead of hemispherical. Given the

very small size and raft-like geometry of the clusters, we have proceeded to normalize reaction rates to the total amount of metal oxide in the sample, assuming every metal cation is a potential active site for C-C coupling. Representative images of other SiO₂-supported catalysts are given in **Figure A2**.



Figure 2.2: High resolution HAADF-STEM images of 2Ta-SiO₂ at two different magnifications (a) and (b).

2.3.2 Diffuse Reflectance UV-Vis Spectroscopy. Diffuse reflectance UV-Vis spectroscopy was used to characterize the supported Ta and Pr catalysts as well as their respective bulk oxides. Direct optical band gaps were calculated from the Tauc plots, an example of which is shown in **Figure A3a**.^[22] **Figure 2.3a** shows the DR UV-Vis spectra of supported Ta catalysts and **Table 2.2** summarizes the absorption band maxima together with the direct band gaps of the samples. Zeolite-supported Ta (2Ta-HBZ) has a Ligand-to-Metal-Charge-Transfer (LMCT) band at 201 nm with an associated direct bandgap of 5.3 eV, which is consistent with reported bandgaps of highly isolated TaO_x species.^[23] An equivalent loading of Ta on SiO₂ (2Ta-SiO₂) shows a longer wavelength LMCT band at 228 nm, with a shoulder at 206 nm. This shorter wavelength shoulder is consistent across all of the SiO₂-supported Ta samples tested. The 2Ta- and 4Ta-SiO₂ catalysts

have a direct bandgap of 5.0 and 4.9 eV, respectively. The higher loaded 4Ta-SiO₂ and 10Ta-SiO₂ have a major LMCT band at 232 nm, but the 10Ta-SiO₂ reveals a substantially lower direct bandgap of 4.5 eV. The well-known quantum size effect associated with small semiconductor oxides clearly demonstrates that low-loaded Ta oxide on SiO₂ (2Ta-SiO₂ and 4Ta-SiO₂) has a smaller cluster size than that on high-loaded 10Ta-SiO₂. All of the supported samples also reveal the quantum size effect relative to a bulk Ta₂O₅ sample, which has a direct bandgap of 4.1 eV (**Table 2.2**). This is consistent with previous reports^[23, 24], and confirms all of our supported samples are highly dispersed oxides. The highest energy bandgap of Ta-HBZ (5.3 eV) suggests that sample has the smallest clusters of Ta oxide in all of our samples and may even be associated with isolated TaO_x species in the zeolite.



Figure 2.3: Normalized DR UV-Vis spectra of **a**) supported Ta catalysts with Ta_2O_5 shown as reference and **b**) supported Pr catalysts with Pr_2O_3 shown as reference (*bands at 272 and 306 nm).

As the cluster size of highly dispersed supported metal oxides may be affected by level of hydration^[25], we examined the spectrum of 2Ta-SiO₂ that was dehydrated in-situ (**Figure A4**). While the LMCT band shifted slightly by 4 nm, the direct bandgap of the 2Ta-SiO₂ was unaffected by dehydration and remained 5.0 eV, as reported in **Table A3**.

Table 2.2. Absorption band positions and direct band gaps of Ta catalysis						
Sample	Band Max (nm)	Direct Band Gap (eV)				
2Ta-HBZ	201	5.3				
2Ta-SiO ₂	228	5.0				
4Ta-SiO ₂	232	4.9				
$10Ta-SiO_2$	232	4.5				
Ta ₂ O ₅	271	4.1				

Table 2.2: Absorption band positions and direct band gaps of Ta catalysts

The DR UV-Vis spectra of the supported Pr samples are shown in **Figure 2.3b** with the absorption maxima and direct bandgaps reported in **Table 2.3**. Zeolite-supported Pr has a major band at 220 nm with a shoulder at 200 nm, while SiO₂-supported Pr has a band at 230 nm. For comparison, a bulk Pr_2O_3 sample shows bands at 272 nm and 306 nm, with a small shoulder at 350 nm. The 4Pr-HBZ sample has the highest direct bandgap at 5.3 eV, followed by 4Pr-SiO₂ at 5.1 eV, and the lowest energy for Pr_2O_3 results in a bandgap of 2.4 eV. As multiple features are evident in the spectrum of Pr_2O_3 in **Figure 2.3b**, the associated bandgaps actually range from about 2.4 to 3.5 eV, shown by Tauc plots in **Figure A3a**. While there are discrepancies in literature regarding the bandgap of Pr_2O_3 , our range of values is similar to the range of previously reported values of 2.4 to 3.9 eV.^[26]

Table 2.5: Absolption band positions and direct band gaps of 11 catalystsSampleBand Max (nm)Direct Band Gap (eV)4Pr-HBZ2205.3 $4Pr-SiO_2$ 2305.1 Pr_2O_3 272, 3062.4 - 3.5

Table 2.3: Absorption band positions and direct band gaps of Pr catalysts

The spectra of SiO_2 -supported Y and La, as well as their bulk oxides, Y_2O_3 and La_2O_3 , are shown in **Figures A5 and A6**. The substantial overlap with the SiO_2 support and absence of distinct features associated with Y and La prevent conclusive evaluation of bandgaps. **2.3.3** X-ray Photoelectron Spectroscopy. To complement results from DR UV-vis spectroscopy, X-ray photoelectron spectroscopy was used to determine the average oxidation state of the transition metal cations on the supported samples. Spectra of representative catalysts are shown in Figure 2.4 and the peak fitting parameters and resulting binding energies are summarized in Tables A5-8. Figure 2.4a shows the Ta 4f region of 2Ta-HBZ and 2Ta-SiO₂. As the O 2s peak appears in the Ta 4f region, the O 2s peak was fixed at 25.4 eV for both 2Ta-SiO₂ and 2Ta-HBZ as determined by the O 2s feature of the corresponding bare support, shown in Figure A7. The binding energy of the Ta $4f_{7/2}$ and Ta $4f_{5/2}$ feature is 27.4 eV and 28.9 eV, respectively, for 2Ta-HBZ, while 2Ta-SiO₂ shows a $4f_{7/2}$ and $4f_{5/2}$ binding energy at 27.2 eV and 29.0 eV, respectively. Both samples show binding energies that are in the range of reported values for Ta in the +5 oxidation state.^[8, 27]

The Y 3p region for 2Y-HBZ and 2Y-SiO₂ is shown in **Figure 2.4b**. Both spectra reveal a Y $3p_{3/2}$ binding energy of 301.7 eV, with 2Y-HBZ showing a Y $3p_{1/2}$ binding energy of 312.7 eV and 2Y-SiO₂ showing a binding energy of 313.6 eV for the Y $3p_{1/2}$ feature. Equal binding energies of the Y $3p_{3/2}$ for SiO₂ and HBZ supported Y samples suggest the Y cation is in a +3 oxidation state on both supports based on previously reported values.^[28]

The spectra of the Pr 3d region of 4Pr-HBZ and 4Pr-SiO₂ are shown in **Figure 2.4c**. In both spectra, Pr $3d_{5/2}$ and $3d_{3/2}$ satellite peaks are observed at lower binding energies relative to the main 5/2and 3/2 peaks, a phenomenon not commonly observed with other transition metal oxides.^[29] In the case of 4Pr-HBZ, the Pr $3d_{5/2}$ satellite appears at 930.1 eV while the main Pr $3d_{5/2}$ feature has a binding energy of 934.1 eV. The binding energy of the Pr $3d_{3/2}$ peak is 954.6 eV and its corresponding satellite is 950.6 eV. A small peak at 958.5 eV has previously been attributed to an additional shake-up peak in the Pr $3d_{3/2}$ spectrum.^[29, 30] For the 4Pr-SiO₂ sample, the Pr $3d_{5/2}$ peak and its satellite are found at 934.2 and 930.3 eV, respectively, with the Pr $3d_{3/2}$ peak occurring at 954.6 eV with its satellite at 950.4 eV. Similar to the HBZ supported sample, 4Pr-SiO₂ has an additional $3d_{3/2}$ shake-up feature at 958.9 eV. The Pr $3d_{5/2}$ binding energies of 4Pr-HBZ and 4Pr-SiO₂ show values that are similar to each other and have been associated with Pr³⁺ and Pr⁴⁺.^[21, 31] Due to this ambiguity, assigning a formal oxidation state to either of the supported Pr samples is rather complex. Nevertheless, we concluded the two samples both have similar speciation of Pr(III) and Pr(IV) based on the similar Pr $3d_{5/2}$ binding energy.

The spectra of La 3d region of 4La-HBZ and 4La-SiO₂ are shown in **Figures 2.4d.** The spectra are composed of four distinct peaks, La $3d_{5/2}$ with its satellite peak as well as La $3d_{3/2}$ and its satellite peak. For 4La-HBZ, the binding energy of the La $3d_{5/2}$ peak is 835.7 eV with a satellite appearing at 839.0 eV, while the binding energy of the La $3d_{3/2}$ peak is at 852.3 eV with a satellite peak at 855.6 eV. Likewise, while 4La-SiO₂ shows binding energies of the La $3d_{5/2}$ and its satellite peaks at 835.5 eV and 838.8 eV, respectively. The La $3d_{3/2}$ peak occurs at 852.2 eV with its satellite at 855.5 eV for the 4La-SiO₂ sample. Both SiO₂ and HBZ supported La samples show La $3d_{5/2}$ binding energies that are in the range for La in a +3 oxidation state.^[32, 33]



Figure 2.4: Photoemission spectra of the **a**) Ta 4f region for 2Ta-SiO_2 and 2Ta-HBZ catalysts. O 2s peak is restrained at 25.4 eV from fitting of respective supports (**Figure A7**), **b**) Y 3p region for 2Y-SiO₂ and 2Y-HBZ catalysts, **c**) Pr 3d region for 4Pr-SiO₂ and 4Pr-HBZ catalysts, and **d**) La 3d region for 4La-SiO₂ and 4La-HBZ catalysts. Spectra were charge referenced to the Si 2p peak at 103.5 eV.^[21]

2.3.4 Cascade Reaction of Ethanol over Physical Mixture of Ag-SiO₂ with M-SiO₂ or M-HBZ. Examples of conversion of ethanol and selectivity to butadiene or butanol with time on stream are shown in **Figures 2.5a and 2.5b** for reactions over 2Ta-SiO₂ or 2Y-SiO₂, physically mixed with Ag-SiO₂. Ethanol conversion over both 2Ta-SiO₂ and 2Y-SiO₂ decreased over the first four hours, after which a steady state was reasonably achieved. Butadiene selectivity shows an initial decrease over the first four hours over 2Ta-SiO₂, but was relatively constant over 2Y-SiO₂. Interestingly, butanol selectivity over 2Y-SiO₂ gradually increased over the same time. To compare the various catalysts in this study, all additional results from the ethanol cascade reaction are reported after four hours on stream as an approximation of steady state performance.

The influence of ethanol conversion on product selectivity over 2Ta-SiO₂ and 2Y-SiO₂ catalysts when physically mixed with Ag-SiO₂ is shown in **Figures 2.5c** and **2.5d**, respectively. The Ag-SiO₂ catalyst alone dehydrogenates ethanol to acetaldehyde (selectivity of 97% at 26% conversion) with no production of any coupling products, as reported in **Table A9**. The conversion in **Figures 2.5c** and **2.5d** was varied by adjusting the catalyst-based space time (total catalyst mass / reactant flowrate) while maintaining the mass ratio of Ag-SiO₂ to M-SiO₂ (1:4). Over the Ta catalyst in **Figure 2.5c**, butadiene selectivity ranged from 12% at low conversion (15%) to 67% at high conversion (70%) revealing a strong dependence on ethanol conversion for this cascade reaction. The simultaneous decrease in acetaldehyde is a major intermediate in the cascade reaction. Selectivity to ethanol dehydration side products, ethylene and diethyl ether, as well as the other products, was below 11% across the range of conversions studied. Over the Y catalyst in **Figure 2.5d** the butadiene selectivity increased from 29% to 46% over conversion range of 12% to 45%, while the selectivity to acetaldehyde decreased from 33% to 19%, after which the selectivities

appeared to plateau. Unlike the reaction over Ta, some butanol was produced over the Y catalyst, with selectivity to butanol decreasing with higher levels of ethanol conversion (**Figure 2.5d**).



Figure 2.5. Performance of multifunctional catalysts in ethanol conversion. Influence of time on stream on the conversion and selectivity to butadiene and butanol over **a**) 2Ta-SiO_2 and **b**) 2Y-SiO_2 when physically mixed with Ag-SiO_2. The influence of ethanol conversion on product selectivity over **c**) 2Ta-SiO_2 and **d**) 2Y-SiO_2 when physically mixed with Ag-SiO_2. Conversion was varied by adjusting space time, maintaining a constant 1:4 mass ratio of Ag-SiO_2 to M-SiO_2 component. TOS = 4 h, 573 K, 6 % EtOH/94 % N_2.

We also tested the effect of Ta or Y loading on the silica support under similar levels of ethanol conversion to remove the influence of ethanol conversion on product selectivity. This was accomplished by maintaining the same amount of Ag-SiO₂ in the mixed catalyst systems as the different loadings of Ta and Y were evaluated. Results from these tests carried out at ~15-20% conversion are summarized in **Tables A10 and A11**. As the loading of Ta on SiO₂ increased from 2 to 10 wt%, the butadiene selectivity increased from 12% to 24%, consistent with expected behavior of added Ta on the support. For the Y catalysts, however, butadiene selectivity was relatively unaffected by Y loading on SiO₂ from 2 to 20 wt%. Instead, butanol selectivity increased from 11% to 17% with increasing Y loading. Clearly, the product distributions derived from Ta and Y catalysts are different.

This distribution of coupling products (butadiene and butanol) suggests the cascade reactions of ethanol are quite sensitive to the acid/base nature of the catalyst component responsible for C-C bond formation. From the comparison of results from Ta and Y catalysts, the silica-supported Ta oxide is expected to be more acidic (producing butadiene and no butanol) than the silica-supported Y oxide (producing both butadiene and butanol). To further explore this concept, we tested the reactivity of supported oxides La and Pr in the ethanol cascade reaction. The product selectivity at relatively constant conversion (~ 14-21%) from ethanol reaction over 4 wt% SiO₂-supported Ta, Y, Pr, and La is found in **Tables A10-A12**. Selectivity results in **Table A12** reveal that butadiene and butanol are produced over both La and Pr.

To complement our studies on the effect of silica-supported transition metal cations (Ta, Y, Pr and La) on ethanol cascade reactions, we also tested the catalytic performance of the same cation series loaded into dealuminated H-beta zeolite. The selectivity to coupling products under comparable

experimental conditions for both silica-supported and zeolite-supported cations is summarized graphically in **Figure 2.6**.

Results in **Figure 2.6a** show that 90% of the coupling products over zeolite-supported Ta was butadiene, which is similar to that observed over silica-supported Ta (86-90% for the two samples shown). For the Y-loaded samples in **Figure 2.6b**, the zeolite-supported Y sample produced more butadiene relative to butanol than the silica-supported Y samples. This trend is also observed when the zeolite supported Pr and La samples are compared in **Figures 2.6c** and **2.6d**, respectively. In summary, butanol was observed over all of the Y, Pr, and La samples, with the selectivity to butanol being higher on the silica-supported catalysts. Moreover, the highest selectivity to butanol (45%) was observed over the silica-supported La catalyst.

Further comparison regarding the strength of Lewis acid and periodic trends can be made from the silica-supported samples in **Figure 2.6**. Moving left to right in row six of the periodic table, including the extended lanthanide series, the acid strength of cations increases. In this case, Ta is the strongest acid cation with the highest fraction of butadiene at 90%, relative to all coupling products, followed by Pr at 51%, while La is the weakest acid of the three with the lowest butadiene fraction at 34%, but shows the highest butanol fraction at 45%. Similarly, when moving up a column in the periodic table, the relative acid strength also increases. Comparing Y and La, the butadiene fraction is higher on Y, 72 % versus 34%, while La has the higher butanol fraction compared to Y, 45% versus 20%, suggesting Y is the stronger Lewis acid between the two cations.



Figure 2.6: Coupling product distribution based on percent selectivity of major coupling products (1,3-butadiene, butanol, as well as C4+ and others) over supported **a**) Ta catalysts, **b**) Y catalysts, **c**) Pr catalysts, and **d**) La catalysts physically mixed with Ag-SiO₂. Conversion was \sim 14-30%, depending on catalyst. Corresponding conversions and product selectivities are shown in **Tables A10-A12**. Total catalyst amount = 0.5 g for M-SiO₂ systems and 0.15 g for M-HBZ systems (0.1 g of Ag-SiO₂ and 0.4 g of M-SiO₂ or 0.05 g of M-HBZ). TOS = 4 h, 573 K, 6 % EtOH/94 % N₂.

While the incorporation of isolated transition metal cations into the zeolite support might increase their Lewis acidity (thus favoring butadiene over butanol), we also suspected that residual acidity in the dealuminated H-beta zeolite might affect the product distribution. To probe the HBZ support itself, a physical mixture of DeAl-HBZ with Ag-SiO₂ was evaluated in the reaction of ethanol. The results presented in **Table A9** reveal 42% selectivity to ethylene and diethyl ether and 52% selectivity to acetaldehyde, indicating there is sufficient residual acidity of the dealuminated zeolite to affect the product distribution. Addition of 4% Na to DeAl-HBZ (4Na-HBZ) was sufficient to neutralize the residual acidity as shown in **Table A9**. Dealumination of the HBZ support removes framework Al sites and introduces silanol nests/hydroxyl groups, which may be responsible for ethanol dehydration side products, ethylene and diethyl ether.^[17] Moreover, although acid treatment removed most of the aluminum in the zeolite, a small amount remained behind. Therefore, residual Brønsted acid sites may also be present in the sample. As the addition of Na to DeAl-HBZ eliminated acid sites without forming coupling sites, the presence of Ta, Y, Pr, or La in the DeAl-HBZ is clearly needed for the C-C bond formation step.

2.3.5 Effect of Support on C-C Coupling Rate. A comparison of apparent site time yield (STY) of C4 coupling products formed at low ethanol conversion over HBZ-supported and SiO₂ supported transition metal cations is shown in **Figure 2.7.** The STY of coupling products formed over 2Ta-HBZ was an order of magnitude greater than that over 2Ta-SiO₂, as illustrated in **Figure 2.7a**. In fact, all of the zeolite-supported catalysts produced coupling products at nearly an order of magnitude greater STY than the corresponding silica-supported catalysts. It should be noted that the site time yields over the Y-loaded catalysts were greater than those over analogous Ta, Pr and La catalysts, as indicated by the different y-axis scale in **Figure 2.7b**.



Figure 2.7: Site Time Yield (STY) of major C4 products (1,3-butadiene and butanol) formed over supported **a**) Ta catalysts, **b**) Y catalysts, **c**) La catalysts and **d**) Pr catalysts that were physically mixed with Ag-SiO₂. Conversion was ~ 14-30%, depending on catalyst mixture. Conversions and product selectivities associated with this figure are presented in **Tables A10-A12**. Total catalyst amount = 0.5 g for M-SiO₂ systems and 0.15 g for M-HBZ systems (0.1 g of Ag-SiO₂ and 0.4 g of M-SiO₂ or 0.05 g of M-HBZ). Time on stream = 4 h, 573 K, 6 % EtOH/94 % N₂.

A previously published study has shown that ethanol dehydrogenation over the same Ag-SiO₂ catalyst operates on the edge of transport limitations at the experimental conditions used in the current study.^[13] To explore the potential role of transport limitations of the coupling reactions in the zeolite pores, the active site density in our most active Y-HBZ catalyst was varied and then evaluated. In this set of experiments, we compared the performance of 1Y-HBZ (loaded into the reactor with twice the mass) to that of 2Y-HBZ, after they were mixed with Ag-SiO₂. Thus, the loading of both the Y and Ag components were held constant in the reactor between the two tests. The rate of C4 product formation versus time on stream is presented for these two cases in **Figure 2.8**. The initial rates of the two cases were similar, suggesting that the coupling rate is strictly proportional to the Y density in the pores, regardless of loading between 1 and 2 wt%. There is a faster deactivation of the 2Y-HBZ catalyst sample, presumably because of the higher concentration of olefins in the pores of the higher loaded zeolite. Nevertheless, the similar initial rates of the two highly active zeolite samples with two different Y loadings, and the much lower rates over all of

the silica-loaded catalysts, suggest that transport limitations are not influencing the rates of C-C coupling reported here.



Figure 2.8: C4 coupling product rate as a function of time on stream for Y-HBZ catalyst systems physically mixed with Ag-SiO₂ representing the effect of varying active site density. Conversion was ~27-38%, depending on catalyst system. Corresponding conversions and product selectivities are shown in **Table A9**. Total catalyst amount = 0.15 g for 2Y-HBZ and 0.2 g for 1Y-HBZ (x2), 0.1 g of Ag-SiO₂ and 0.05 g of 2Y-HBZ or 0.1 g of 1Y-HBZ (x2), 573K, 6 % EtOH/94 % N₂.

2.3.6 Reaction of 2-propanol over M-SiO₂ and M-HBZ. The reaction of 2-propanol to propene and acetone was used as a probe of the acid and base sites on the various catalysts. The use of 2-propanol decomposition as a measure of acid strength has previously been reported for a variety of bulk oxides.^[34] Although acidic oxides favor dehydration of 2-propanol to propene and basic oxides favor dehydrogenation of 2-propanol to acetone, the rate of propene formation can be correlated to acid strength.^[34] Results from 2-propanol reactions over SiO₂-supported, 4 wt% Ta, Y, Pr and La, are summarized in **Table 2.4.** All of the catalysts produced mostly propene from 2-propanol dehydration, but low levels of acetone were sometimes observed. Selectivity to propene was highest over Ta (100 %), followed by Y (98 %), Pr (91 %) and La (85 %). Thus, Ta appears

to be the most acidic of the supported oxides, producing no acetone, while La appears to be the least acidic of the supported oxides, producing acetone with 15% selectivity. The STY of propene followed the same trend as selectivity, with the STY over Ta being greater than that over La by more than an order of magnitude (**Table 2.4**). Based on the results from both selectivity and rate of the 2-propanol reaction, the SiO₂-supported Ta and Y oxides are stronger Lewis acid catalysts compared to the analogous Pr and La catalysts.

Catalyst	Conversion (%)	Selectivity (%)		STY (mol i)·(mol M) ⁻¹ (s) ⁻¹	
		Propene	Acetone	Propene $(x10^{-3})$	Acetone (x10 ⁻⁵)
4Ta-SiO ₂	5.7	100	0	3.8	-
4Y-SiO ₂	7.5	98	2	2.0	3.4
4Pr-SiO ₂	1.3	91	9	0.3	4.1
4La-SiO ₂	0.8	85	15	0.2	3.0

Table 2.4: Decomposition of 2-propanol over M-SiO₂ catalysts

Catalyst amount = 0.05 g of M-SiO₂, TOS = 11 h, 523 K, 3 % 2-propanol/97 % N₂ We attempted to use 2-propanol reactions to characterize the transition metal cations in zeolites, but the reaction produced exclusively acid-catalyzed propene as well as side product isopropyl ether at high rates. Evidently the residual acidity of the zeolite samples obscured the reactivity of the Lewis acid cations. A complete description of these experiments can be found in the Supporting Information.

2.4 Discussion

The distribution of coupling products from the ethanol cascade reaction is expected to be related to the Lewis acid strength of the catalyst. **Figure 2.9** shows a correlation of the butadiene in the C4 coupling products (butadiene + butanol) to propene STY over the four silica-supported

transition metal cations. This correlation supports the concept that stronger Lewis acid cations produce more butadiene, and conversely, weaker Lewis acid cations produce more butanol.



Figure 2.9: Fraction of 1,3-butadiene in the C4 product distribution from the ethanol cascade reaction (Total catalyst amount = 0.5 g, 0.1 g of Ag-SiO₂ and 0.4 g of M-SiO₂, TOS = 4 h, 573 K, 6% EtOH/94 % N₂) correlated to the propene STY from derived 2-propanol reaction over *M*-SiO₂ catalysts (0.05g of M-SiO₂, TOS = 11 h, 523 K, 3 % 2-propanol/97 % N₂).

Whereas the Lewis acidity of the supported cations seems to account for differences in the final C4 product selectivity, they do not account for the observed differences in the coupling rate. For example, comparing the strongest and weakest Lewis acid cations in our series (i.e., Ta to La), the C4 coupling rate over silica-supported Ta and La was nearly the same, as depicted in **Figures 2.7a** and **2.7d**. The major difference in rate is not the result of cation identity, but because of the support structure, SiO₂ or HBZ. In general, the C4 coupling rate (or STY) was an order of magnitude greater over HBZ catalysts compared to their SiO₂ counterparts. As our results from XPS indicate the average oxidation state of each type of transition metal cation does not depend on the support, we speculate the confined environment of the zeolite micropore accounts for some of the observed rate acceleration. Adsorption of acetaldehyde in the zeolite micropores may enhance the local

concentration of this key reaction intermediate above that adsorbed in the larger pores of silica, which would accelerate the bimolecular aldol condensation reaction that forms the C4 coupling products. The confinement effect has been previously reported as an explanation for the higher rates of self-aldol condensation of aldehydes over Y-HBZ compared to Y-SiO₂ catalysts as reported by Yan et al.^[35] Similarly, Dai et al. attributed structural confinement to the higher butadiene productivity that was five times higher on their Zn-Y-Beta compared to Zn-Y-SiO₂.^[16] However, Qi et al. suggested the higher rate of C-C coupling over Y-Beta compared to Y-SiO₂ was due to the structural environment of hydroxyl groups around the Y active site.^[17] In an alternative explanation, Zhang et al. used a spectroscopic method with adsorbed pyridine to count Lewis acid sites and propose that a higher Lewis acid site density over their tri-metallic Cu-Zn-Y-Beta relative to its SiO₂ analogue accounts for their observed enhancement of C-C coupling rate in the zeolite catalyst.^[18] We cannot rule out a potential promoting effect of better site isolation of the cations in the zeolite micropore compared to cations on silica, as revealed by the DR UV-vis spectra in Figure 2.3. Additional work is needed to prepare site-isolated cations on silica to better compare to the zeolite supported samples.

Referring to the network in **Figure 2.1**, the type of support appears to affect the overall rate of C-C coupling to form intermediate crotonaldehyde via aldol condensation. The Lewis acid strength of the cation then influences primarily the distribution of final coupling products through reaction of crotonaldehyde via hydrogen transfer and dehydration, according results in **Figures 2.6, 2.7**, and **2.9**.

We found it interesting that Y catalysts always exhibited the greatest rates of formation of C4 coupling products, whether supported on SiO_2 or HBZ, compared to the Ta, Pr or La analogues. The nature of the higher rate of coupling with Y certainly warrants further study.

2.5 Conclusions

A catalyst system comprising a physical mixture of Ag-SiO₂ and Lewis acid cations (Ta, Y, Pr, or La) supported on either SiO₂ or HBZ was used to directly compare the performance of the four cations and two different supports in the conversion of ethanol to butadiene without the interference of Ag on the characterization of the supported cations. The DR UV-vis spectra of supported Ta and Pr oxides revealed a quantum size effect relative to their corresponding bulk oxides and the observed spectral shifts were greatest for the zeolite-supported samples, consistent with the smallest cluster sizes or even that isolated cations were achieved in the zeolite pores. Nevertheless, results from XPS confirmed the oxidation state of the supported cations was unaffected by difference in site isolation or cluster size.

The distribution of the observed C4 products formed from ethanol correlated to the Lewis acid strength of the supported cation. For the silica-supported samples, the highest fraction of C4 products to butadiene was observed over Ta whereas the lowest fraction to butadiene was observed over La. Results from 2-propanol decomposition to propene (both rate and selectivity) were consistent with the expected ranking of cation Lewis acid strength, with Ta being the strongest and La being the weakest of the cations studied.

The zeolite-supported cations demonstrated an order of magnitude higher rate of C-C coupling compared to their analogue SiO_2 supported cations, with the selectivity depending on the identity of the Lewis acid cation, as described above. Although the reasons for the observed rate enhancements remain unclear, zeolites should continue to be explored as unique microporous supports for conversion of bioethanol to longer carbon chain products.
2.6 Acknowledgements

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Chapter 3: Influence of Domain Size and Support Composition on the Reducibility of SiO₂ and TiO₂ Supported Tungsten Oxide Clusters

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Quantum chemical calculations presented in this chapter were performed by Anukriti Shrestha under the guidance of Professor Christopher Paolucci. X-ray absorption spectroscopy and analysis was performed by Dr. Colby A. Whitcomb.

Abstract

Supported tungsten oxides are widely used in a variety of catalytic reactions. Depending on the support, the cluster size, oxidation state, reducibility and speciation can widely differ. When promoted with a platinum group metal (PGM), the resulting spillover of hydrogen may facilitate the reduction of supported tungsten oxide species, depending on the support. High resolution STEM imaging showed nanometer scale WO_x clusters on SiO₂ and highly dispersed species on TiO_2 . Results from H₂-temperature-programmed reduction (TPR) showed the presence of Pd lowered the initial reduction temperature of silica-supported WO_x species but did not affect that of titania-supported WO_x. In situ X-ray photoelectron and absorption spectroscopies (XPS and XAS, respectively) in 5% H₂/N₂ showed the W atoms in SiO₂-supported WO_x species reduce from a +6 oxidation state to primarily +5, while the fraction of W in the +5 oxidation state was relatively unaffected by reduction treatment of titania-supported WOx. Ab initio quantum chemical calculations revealed the lack of change in the oxidation state of W for titania-supported WO_x is attributed to charge delocalization on the surface atoms of the titania support, which does not occur on silica. Moreover, modeling results suggest the formation of Brønsted acid sites on larger aggregates of WO_x on silica and all cluster sizes on titania at < 600 K in the presence of H₂. This work provides experimental and theoretical insights into the nature of supported tungsten oxide clusters under conditions relative to various catalytic reactions.

3.1 Introduction

Supported tungsten oxide catalysts have gained significant attention in the field of heterogeneous catalysis due to their widespread application in various catalytic processes such as dehydrogenation of alcohols, selective catalytic reduction of NO_x, oxidative coupling of methane, isomerization of alkenes and alkanes, and dehydration of alcohols.^{1, 2} Supported tungsten oxide catalysts can be promoted with platinum group metals (PGM) which are known to aid in the dissociation of H₂ into atomic hydrogen.³ Spillover of atomic hydrogen can promote the reduction of the supported metal oxide (i.e., WO_x), and is suggested to play a crucial role in enabling the reduction of carboxylic acids to alcohols and aldehydes.^{4, 5} During these reactions, H₂ can participate as a reactant⁶ and (or) be involved in creating the active site(s) on the catalyst.^{4, 7, 8} The identity and density of these active sites are affected by the nature of the support, ⁹ and our goal here is to discern how the WO_x species transform on chemically diverse supports (i.e., TiO₂ and SiO₂) when atomic hydrogen is available from spillover.

Hydrogen spillover from PGMs to WO_x has been shown to generate actives sites for catalytic reactions involving H₂ across a variety of supports. Hydrogen spillover from Pt to WO_x on a Pt-W-TiO₂ catalyst was shown by Raman spectroscopy to consume the W=O functional group and generate Brønsted acid sites. Reduction of W^{6+} was confirmed with X-ray photoelectron spectroscopy (XPS), which showed an increase in the W^{5+}/W^{6+} ratio.⁴ Similarly, SiO₂-supported Pd-W show reduction of W^{6+} to W^{5+} from X-ray absorption spectroscopy (XAS) under reaction conditions for the reduction of propionic acid to propanol in H₂.⁵ Inverse Pt-W catalysts, where WO_x is deposited onto silica-supported Pt, show evidence of W reduction and generation of Brønsted acid sites at 673 K, in contrast to a W-SiO₂ catalyst that showed a maximum consumption at 1100 K in the profile of temperature-programed reduction (TPR).⁷ Titania-supported Pd-W

catalysts are also active for the reduction of propionic acid to propanol in H_2 ,⁵ which suggests that reduction of W may also occur on these materials, similar to the reduction of Ti⁴⁺ to Ti³⁺ observed by XPS for Pd supported on TiO₂ during exposure to H_2 .¹⁰

While there is agreement in literature regarding the ability of PGM-promoted tungsten oxides to catalyze a variety of reactions, the nature of the active site(s) is still debated, especially on different supports. Numerous experimental techniques have been used to investigate supported WO_x catalysts and computational investigations have indicated that formation of Brønsted acid sites on WO_x catalysts is influenced by reaction conditions.¹¹⁻¹³ The composition of the support can also alter the nature of the active site. For instance, a ZrO₂ support can increase the Brønsted acidity of larger WO_x clusters.^{14, 15} Similarly, computational investigations have reported that monomeric WO_x is the preferred stable configuration on titania support.^{16, 17} whereas trimers are preferred on a Pt support.¹² Hence, the support composition and domain size of supported WO_x catalysts is inextricably linked to its catalytic activity.

Herein, we aim to better understand the molecular configuration/structure, charge states, as well formation of acid sites on supported tungsten oxide clusters as a function of experimentally relevant reaction conditions such as temperature and dihydrogen pressure through experimental and computational approaches. We explore the tungsten oxide speciation and reducibility on two different supports: TiO₂, a reducible support and SiO₂, a non-reducible support. By using Pd to facilitate the generation of atomic hydrogen (in an H₂ environment) and thus hydrogen chemical potential via the spillover effect on supported tungsten oxide species, we relate our experimental work to the computational results. We show tungsten oxide cluster sizes vary depending on the support, with TiO₂-supported WO_x clusters being much smaller than their SiO₂ analogs. Furthermore, the W atoms in WO_x species supported on SiO₂ are able to reduce from a +6 to a

primarily +5 oxidation state, while the fraction of W atoms being reduced on the TiO_2 support was minor, even in the presence of Pd. Density Functional Theory (DFT) calculations for different cluster sizes on the two supports revealed that the charge delocalization on the titania support prevents significant reduction of the supported WO_x cluster. Moreover, quantum chemical calculations suggest that, at conditions relevant for catalysis, the presence of H₂ forms Bronsted acid sites on the WO_x clusters.

3.2 Methods

3.2.1 Sample Synthesis. High-purity SiO₂ (Sigma-Aldrich, Davisil 635, 60 Å, 480 m² g⁻¹, 150-250 μ m) was used for the SiO₂-supported samples. For acid-treated SiO₂ (AT-SiO₂) samples, SiO₂ was first treated in 13M HNO₃ at 373 K for 20 h, washed with distilled, deionized (DDI) water to a pH of 5-6, and dried at 393 K overnight. Silica-supported W samples were synthesized by incipient wetness impregnation, in which a desired amount of ammonium metatungstate (Aldrich, 99.99%), was mixed with DDI water to achieve a solution that was equal to the pore volume of the support, which was then added drop-wise onto the support until the point of incipient wetness. Samples were dried overnight in air at room temperature, followed by a 2 h drying period in air at 393 K, and thermally treated at 923 K in 100 cm³ min⁻¹ flowing medical air (Praxair) for 4 h. For Pd-W-(AT)-SiO₂ samples, the same incipient wetness procedure was followed with previously synthesized W-SiO₂ samples, using tetraaminepalladium(II) nitrate solution (10 wt% in H₂O, Sigma-Aldrich) as the Pd precursor with the same drying and thermal treatment conditions as well. Samples are labeled as (Pd)-xW-SiO₂ where x is the nominal weight percent of W.

Titania-supported samples used mixed phase TiO₂ (Sigma-Aldrich, P25 nanopowder, 21 nm), and Rutile-TiO₂ (R-TiO₂) (Sigma-Aldrich, nanopowder, <100 nm, 99.5%) as the supports for (Pd)-

xW-P25-TiO₂ and (Pd)-xW-R-TiO₂ samples. Titania supports labeled P25-TiO₂ without any Pd and/or W designate TiO₂ materials after a thermal treatment at 923 K in 100 cm³ min⁻¹ flowing medical air (Praxair) for 4. Synthesis of Pd and/or W-incorporated samples utilized fresh P25-TiO₂ without any prior pretreatment. The same IWI procedures were followed as with the SiO₂ supported samples. The samples were then dried and thermally treated as previously described for the SiO₂-supported samples. Reference materials WO₃ (Alfa Aesar, 99.998 %), WO₂ (Alfa Aesar, 99.9 %), and Na₂WO₄·2H₂O (Sigma, \geq 99.0 %) were used as received from suppliers. For the 1Pd-WO₃ sample, a similar IWI procedure was followed as for the W-SiO₂ and W-TiO₂ supported with the same Pd precursor and bulk WO₃ as the support. Analogous drying and calcination procedures as mentioned previously were used as well.

3.2.2 Sample Characterization. Dihydrogen TPR was carried out with a Micromeritics AutoChem II 2920 system equipped with a TCD detector. Non-supported samples, Pd-WO₃, WO₃, and WO₂, were not exposed to any pretreatment and 0.05 g of sample was used. For SiO₂ and TiO₂-supported samples, 0.3 g of sample were used and a sample was first heated to 773 K under O_2 and cooled to 323 K prior to introduction of the reducing gas mixture of 5% H₂ in Ar at 30cm³ min⁻¹. Temperature of the sample was ramped at 10 K min⁻¹ to 1223 K and held for 20 min.

Diffuse reflectance (DR) UV-Visible spectra were collected on a PerkinElmer Lambda 850+ UV-Vis spectrometer with a Harrick Praying Mantis Diffuse Reflection Accessory. Polytetrafluoroethylene (Sigma-Aldrich, powder, >40 μ m) was used as the reflectance standard, with spectra recorded from 190 to 600 nm. Direct optical band gaps were calculated from Tauc plots¹⁸ with an example provided in **Figure B1**. In situ XPS measurements were performed using a PHI VersaProbe III spectrometer equipped with Monochromatic Al K-alpha X-rays (1486.6 eV) and a hemispherical analyzer. A pass energy of 23 eV and an X-ray beam size of 100 µm were used for high-resolution region scans. An internal electron flood gun (1 ev) and low energy Ar ion gun were utilized during data collection as neutralization systems. Samples were pressed into a Cu grid and exposed to a reducing gas mixture of 5% H₂/N₂ flowing at 30 cm³ min⁻¹ inside a reaction chamber, and the temperature was ramped at 40 K min⁻¹ until the desired set point, followed by a hold for 20 min. Following a cool down to ambient temperature, sample transfer from the reaction chamber to the analysis chamber was performed under high vacuum.

High temperature reduction of certain samples did not provide a characteristic C1s peak. Instead, the Si 2p peak at 103.5 eV or Ti 2p peak at 458.7 eV was used as a charge reference.¹⁹ The binding energy difference for the W4f_{7/2} peak between reference WO₃ and WO₂ has been reported to be in the range of 2.8-3.0 eV, while the difference between WO₃ and W metal is in the range of 4.3-4.5 eV.²⁰⁻²² The difference between the W 4f_{7/2} and W 4f_{5/2} peaks was kept constant at 2.18 eV, thus only the 7/2 peak values in subsequent figures are provided for brevity. The Ti 3p peaks in the W 4f region were constrained based on the position of the TiO₂ support Ti 3p peaks following the same reduction procedure. All peak locations and fitting parameters can be found in the SI.

X-ray absorption spectroscopy (XAS) at the W L_{III}-edge was performed using beamline 8-ID at the National Synchrotron Light Source II at Brookhaven National Lab operating at 3.0 GeV and a beam current of 400 mA.²³ A W metal foil (EXAFS Materials) was used as a reference for the W (11544.0 eV) L_{III} edge. Transmission studies were performed using a high-throughput cell with a temperature controller and Kapton windows as previously described.²⁴ Although the silica samples were able to get a reasonable edge jump in transmission mode, the absorption of the TiO₂ required

that fluorescence data be collected. The fluorescence cell utilized quartz capillaries (1.5 mm diameter, 75 mm length, Friedrich & Dimmonck, Inc) with samples added to the glass tube and fluorescence photons collected on a Passivated Implanted Planar Silicon (PIPS) detector. Initially a flow rate of 10 cm³ min⁻¹ of He is used for the pre-TPR run while 20 cm³ min⁻¹ of 5% H₂/N₂ was flowed for the reduction experiments at high temperature and upon cooling to room temperature after TPR. The XAS spectra were subsequently processed using the Demeter software package.²⁵ The oxidation state of the W in each sample was estimated using the L_{III} edge. The edge at a step height of unity was normalized using the reference foil collected for each sample to account for any deviations among the samples and ensure that there were no artifacts from the white line. Tungsten foil (EXAFS Materials), powdered WO₂ (Alfa Aesar, 99.9 %), and powdered WO₃ (Alfa Aesar, 99.998 %) were used as oxidation state standards at the W L_{III} edge. The powders were pressed before addition to Kapton tape for placement into the beam path for measurement. The W L_{III}-edge XANES for the W foil, WO₂, and WO₃ are plotted in Figure B17. The edge energy evaluated at the unity value of the absorption coefficient of the standards was used to make a calibration curve that was utilized to estimate the changes in the oxidation state of the W in the sample during reduction.

X-ray diffraction (XRD) patterns were obtained on a PANalytical Empyrean diffractometer using Cu-K α radiation (λ of 1.54Å) generated at 45 kV with a 40 mA incident X-ray source. Scans were collected in the range of $2\theta = 15-80^{\circ}$ with a 0.015° step size. Rietveld refinement was performed with the Maud program.

X-ray fluorescence (XRF) measurements were performed by Horiba Scientific (Piscataway, NJ) with an XGT-9000 XRF analytical microscope equipped with a 50W Rh anode X-ray tube. Spectra were collected in a partial vacuum over an area of 12.5 mm², an energy resolution of less than 143

eV at Mn-K α , and an accelerated voltage of 50 keV. Component concentrations were calculated using the Fundamental Parameters Method.

The HAADF-STEM images were taken on a Thermo Fisher Scientific Themis Z transmission electron microscope operating at 200 kV and equipped with a monochromator and probe correction. The STEM-HAADF detector (Fischione) collection angle was set to 50-200 mrad at 115 mm camera length. Samples were slurried either in methanol or hexane and deposited on lacey or holey carbon films supported on copper grids.

3.2.3 DFT Calculations. DFT calculations were conducted using the Vienna Ab-Initio Simulation Package (VASP),⁵⁴ version 5.4.4. We used the strongly constrained and appropriately normed (SCAN) functional to describe the exchange-correlation potential and a plane wave cutoff energy of 400 eV. Structures optimized using the SCAN functional are used to generate phase diagrams in Figures B26 and B27 for different size tungsten oxide clusters and their oxidation states under varying temperature and H₂ pressure conditions. However, GGA functionals like SCAN do not necessarily have reliable accuracy for the charge distribution on oxides.²⁶ To address this, we incorporate a more accurate hybrid functional, Heyd-Scuseria-Ernzerhof functional (HSE06). For structures that have the lowest free energies at the experimental conditions (600 K - 1000 K in 5%) H_2 – indicated by dashed line in Figures B26 and B27) we performed single point energy calculations using the HSE06. Phase diagrams in Section 3.3.3.1 and 3.3.3.2 were generated using HSE06 but remain similar to those generated by SCAN, with the main difference being the density of states, as described in Section B.4. Initial structures for the bulk phases were taken from the Materials Project database.²⁷ For bulk structure optimizations we used the Monkhorst-Pack k-point mesh reported in Materials Project.²⁷ Cell vectors for bulk structures were optimized. Vibrational contributions to free energy were neglected since we expect them to be similar across the materials

studied here. Stoichiometric slabs were constructed from optimized bulk cells using the Python Materials Genomic (*Pymatgen*) package, *Slabgenerator* function. Each slab contains at least a 10 Å thick layer of atoms. To prevent interactions between surfaces, a vacuum space of 12 Å was added for each slab. The convergence criteria for all calculations (bulk and slab) were electronic energies converged to 10^{-6} eV and atomic forces to less than 0.03 eV/Å. The k-point mesh for each slab (in the *x* and *y* directions) was estimated using the k-points per reciprocal Å for the bulk structure and rounding up, and a single k-point was used in the *z* direction (where vacuum was added). The reference energy used for H₂ is $E_{H_2}^{ref} = -6.69$ eV and H₂O is $E_{H_20}^{ref} = -14.21$ eV. We utilized DFT calculations with the same parameters described above with HSE06 functional to compute these energies.

To determine the most thermodynamically stable WO_3 speciation on the support (MO_2 , M=Ti or Si) at different hydrogen conditions, we evaluated the free energy of all the structures that we consider (Section 3.3.3.1 and Section 3.3.3.2) and calculate it as:

$$MO_2WO_3 + (x + 0.5y)H_2 \rightarrow MO_2WO_{3-x}H_y + xH_2O$$

$$\Delta G(\mu_{\rm H_2}, \mu_{\rm H_2O}) = E_{\rm MO_2WO_{3-x}H_y} - E_{\rm MO_2WO_3} - y\left(\frac{\mu_{\rm H_2}}{2}\right) + x(\mu_{\rm H_2O} - \mu_{\rm H_2})$$

 $E_{MO_2WO_{3-x}H_y}$ is the DFT-computed energy of the given supported monomer, $E_{MO_2WO_3}$ is the energy of the WO₃ monomer on either support. Here, *x* represents the number of O atoms removed and *y* represents the number of H atoms added. We define $\mu_{H_2}^{ref} = E_{H_2}^{ref}$ and $\mu_{H_2O}^{ref} = E_{H_2O}^{ref}$.

The amorphous nature of the silica support presents challenges for modeling, requiring an ensemble of molecular models^{28, 29} rather than a single structure. To avoid this complication, but preserve the electronic properties of SiO₂, we used the β -crystabolite-SiO₂ (001) surface as a

surrogate model, which has been previously used as a reasonable computational model for amorphous silica.³⁰ We obtained the bulk β -crystabolite-SiO₂ structure from the Materials Project database and subsequently optimized its cell vectors and atomic positions. Pymatgen³¹ was used to generate the (001) symmetric slab from the optimized bulk structure, and the slab was then hydroxylated by adding H atoms to each terminal O atom (8 on each side). The atomic positions of the slab were then optimized, and the bottom 10Å of the slab were fixed for the subsequent calculations.

3.2.4 Basin-hopping Global Optimization. Since there are several ways to graft a WO₃ cluster onto a support, we used a global optimization scheme with Basin-hopping³² to automate the grafting process and check for low energy configurations. Basin-hopping is a global optimization technique that randomly perturbs the coordinates of the atoms in the structure and performs a local optimization at each step for a given number of iterations. After every iteration, the coordinates of the structure are either accepted or rejected based on the Metropolis criterion. If the energy returned by the local DFT geometry optimization is lower than that in the previous step, the coordinates are accepted. If the energy is higher, then the probability of accepting the move is calculated using a Boltzmann distribution. For the supported clusters, at every iteration, each atom in the monomer is translated by a random distance, up to 5 Å in the x and y direction and 0.5 Å in the z direction. The surface atoms are not randomly perturbed but are allowed to relax during the local geometry optimization. We used this scheme with 40 iterations to allow the cluster to navigate across different configurations on the surface to increase the probability that we find the lowest energy configuration. Basin-hopping is used to find the lowest energy configuration for the W monomer, dimer and trimer supported on titania. The silanol groups on the silica surface introduce additional

complexity, constraining the cluster movement. Hence, we do not use Basin-hopping optimization for the silica-supported catalysts.

3.2.5 Bader Charge Analysis and Density of States. Bader charge analysis was performed using the method developed by Henkelman et al.^{33, 34} We assign formal oxidation states of +6 and +4 to the charge densities of WO₃ and WO₂, respectively. These states were used as a calibration to assign oxidation states to W in the supported clusters. The charge analysis provides a quantitative understanding of the electron distribution and oxidation state changes occurring during the interaction of tungsten with the supports. We used vaspkit³⁵ to analyze and visualize the density of states (DOS) of different supported W clusters. The DOS analysis provides insights into the electronic structure by presenting the distribution of electronic states across the energy levels.

3.3 Results and Discussion

3.3.1 Tungsten Oxide Cluster Size on SiO₂ and TiO₂ Supports. To provide a visual representation of the tungsten oxide cluster sizes on SiO₂ and TiO₂ supports we characterized samples with high resolution HAADF-STEM following W deposition and pretreatment in flowing dry air at 923 K. Figures 3.1 and 3.2 show HAADF-STEM images of SiO₂- and TiO₂-supported W samples, respectively (samples are labeled as (Pd)-xW-SiO₂ where x is the nominal weight percent of W). Figure 3.1a shows WO_x nanoparticles and small clusters on the 6W-SiO₂ sample, which are primarily in the range of 1 to 3 nm in diameter. The acid-treated silica sample 2W-AT-SiO₂ shown in Figure 3.1b reveals both a lower number density as well as smaller average WO_x size relative to 6W-SiO₂. Additional images of silica-supported samples are provided in the Appendix (Figure B2).



Figure 3.1: High resolution HAADF-STEM images of a) 6W-SiO₂ and b) 2W-AT-SiO₂. To supplement the characterization of tungsten oxide cluster sizes derived from the HAADF-STEM images for the SiO₂ supported samples, we used diffuse reflectance (DR) UV-Vis spectroscopy (for TiO₂-supported W, background adsorption of the TiO₂ support precludes similar analysis, Figure B3). Figure 3.2 shows UV-Vis spectra for the reference bulk WO₃ standard and SiO₂-supported W samples, with Ligand-to-Metal-Charge-Transfer (LMCT) band absorption maxima and direct optical bandgaps for corresponding samples tabulated in Table B2. The SiO₂supported tungsten oxide samples show a distribution of LMCT bands and direct bandgaps. The 2W-AT-SiO₂ sample has an LMCT band at 221 nm, with a corresponding bandgap of 4.8 eV, consistent with fairly isolated monomeric WO_x species^{36, 37} such as those in Na₂WO₄ which has a bandgap of 5.1 eV (Figure B4 and Table B2). However, the broad tail of the band suggests the presence of additional larger oxide clusters, consistent with the small clusters observed by HAADF-STEM in Figure 3.1b. The 6W-SiO₂ sample shows a higher wavelength absorption band at 270 nm with a direct bandgap of 4.0 eV, which suggests the presence of WO_3 nanoparticles with some potentially distorted yet isolated sites,³⁸ aligning with the HAADF-STEM images in Figure

3.1. Additional images and DR UV-Vis spectra can be found in the SI. For comparison, the reference WO₃ bulk standard shows multiple features in the spectra with the main band at 378 nm corresponding to a direct bandgap of 2.8 eV. The DR UV-Vis results of SiO₂-supported W samples arise from the well-known quantum size effect of semiconductor oxides. High bandgaps, such as those of 2W-AT-SiO₂, are representative of smaller oxide cluster sizes, while lower bandgaps, such as those of 6W-SiO₂ and WO₃, are representative of larger clusters and bulk oxide species, respectively.



Figure 3.2: Normalized DR UV-Vis spectra of silica-supported W materials and reference WO₃.

Unlike the WO_x clusters supported on SiO₂ in **Figure 3.1**, TiO₂-supported WO_x species are subnanometer in size regardless of the titania crystal phase (**Figure 3.3a** shows the P25-TiO₂ support, which is primarily anatase). The WO_x species are highly dispersed on both TiO₂ supports, with predominately low W nuclearity (e.g., W monomers, dimers, trimers, etc.) WO_x clusters present. Additional images with higher resolution and lower W loading supported on P25-TiO₂ are provided in **Figure B5**. Results from microscopy indicate WO_x forms larger W domains on the untreated SiO_2 support than on either TiO_2 support, consistent with results from *ab initio* thermodynamic modeling at synthesis conditions described below (Sections 3.3.3.1 and 3.3.3.2).



Figure 3.3: High resolution HAADF-STEM images of a) 6W-P25-TiO₂ and b) 6W-R-TiO₂.

3.3.2 Reducibility of Tungsten Oxide on SiO₂ and TiO₂ Supports

3.3.2.1 H₂-**TPR.** We used dihydrogen TPR to quantify the reducibility of SiO₂- and TiO₂supported WO_x species and the effect of hydrogen spillover from Pd. **Figure 3.4a** shows the TPR profiles of 6W-SiO₂ and 1Pd-6W-SiO₂. Reduction of the WO_x species on 6W-SiO₂ begins at 915 K and continues to 1223 K. The 1Pd-6W-SiO₂ sample, and the 1Pd-6W-P25-TiO₂ sample (**Figure 3.4b**), show an inverse peak at 350 K associated with the decomposition of the β-phase Pd hydride.³⁹ Initial reduction of WO_x species begins around 450 K, with two peaks at 700 K and 915 K attributed to the spillover of atomic hydrogen from Pd. Our results are consistent with platinum group metals decreasing the initial reduction temperature of reducible metal oxides, which has been shown for a variety of comparable systems (*vide supra*), such as Pd-promoted MoO₃ catalysts.⁴⁰ Further reduction of tungsten oxide species continues to 1223 K, similar to the 6W-SiO₂ sample.



Figure 3.4: Temperature-programed reduction profiles of **a**) $1Pd-6W-SiO_2$ and $6W-SiO_2$ samples and **b**) $1Pd-6W-P25-TiO_2$, $6W-P25-TiO_2$, and $6W-R-TiO_2$ samples with a ramp rate of $10 \text{ K} \cdot \text{min}^{-1}$ to 1223 K and hold for 20 min under a flow of 5% H₂/Ar at 30 cm³min⁻¹.

The TPR profiles of 6W-R-TiO₂, 6W-P25-TiO₂, 1Pd-6W-P25-TiO₂, and the bare P25-TiO₂ support are shown in **Figure 3.4b.** All three samples show an initial reduction at 600 K, which is at lower T than that of the SiO₂-supported samples. However, this is the same temperature where the P25 and R-TiO₂ supports also begin to consume H₂ (**Figures 3.4b and B6**). Based on the reduction profiles of TiO₂-supported WO_x species and those of the bare titania supports, the influence of Pd on the reducibility of WO_x is difficult to discern, although a greater amount of H₂ consumption is evident between 1000 K and 1200 K. The hydrogen consumption associated with the reducible titania support prevents determination of the exact hydrogen uptake by the WO_x species, however it is evident that the addition of WO_x species on both TiO₂ supports allows for a higher consumption of H₂ during TPR than the bare support. Conversely, the 6W-SiO₂ sample showed a hydrogen consumption of 0.8 mol H₂/mol W while the 1Pd-6W-SiO₂ sample showed 1.1 H₂/mol W (**Table B3**). A lower W loading on the 3W-SiO₂ sample showed a hydrogen consumption of 0.9 mol H₂/mol W (**Figure B7**), while the 2W-AT-SiO₂ sample had a hydrogen consumption of 0.5 H₂/mol W (**Figure B8**). Based on these values, the WO_x species on the SiO₂ supported samples *do not* reduce to W metal under the conditions of the TPR. On the contrary, the reference oxides WO₃ and WO₂ (**Figure B9**) consumed 2.8 and 1.9 mol H₂/mol W at identical conditions, respectively, suggesting reduction to primarily W metal. These results indicate that SiO₂-supported tungsten oxides reduce to intermediate oxidation states between +6 and 0.

3.3.2.2 In situ X-ray Photoelectron Spectroscopy. To determine the resulting oxidation states of supported tungsten oxide species following various thermal treatments in H₂ we used *in situ* XPS. Tungsten oxides exist in various stoichiometries, with WO₃ having W in a +6-oxidation state the most common. Removal of some oxygen from WO₃ results in WO_{3-x}, which is a non-stoichiometric oxide with a W oxidation state between +6 and +4, commonly denoted as +5.^{20, 41, 42} Further removal of oxygen forms WO₂, with a +4 oxidation state, followed by W⁰ metal.^{20, 41} Figures 3.5a-c show photoemission spectra for the W4f region of 6W-SiO₂ and 1Pd-6W-SiO₂ samples following a reducing treatment in 5% H₂/N₂ at 600, 800 and 1000 K, respectively. The W4f_{7/2} peak positions corresponding to specific oxidation states, together with areas of each species derived from curve fitting, were used to assign sample oxidation states following these treatments. After treatment at 600 K, the spectrum of 6W-SiO₂ shows a W 4f_{7/2} peak at 36.7 eV, which is consistent with an oxidation state of +6 in WO₃²⁰, suggesting all the tungsten oxide species are initially in a +6 oxidation state. After the same reducing treatment, 1Pd-6W-SiO₂ shows two W4f_{7/2} peaks at 36.6 eV and 35.4 eV, ²⁰ corresponding to 55% of W⁶⁺ and 45% of W⁵⁺. Additionally, **Figure B10** shows

the Pd was completely reduced to Pd⁰ by 600 K in H₂. Further treatment at 800 K on the 6W-SiO₂ sample shows reduction of the W species with 37% W⁶⁺ and 63% W⁵⁺, while 1Pd-6W-SiO₂ shows a distribution of 23% W⁶⁺ and 77% W⁵⁺ as shown in **Figure 3.5b**. Upon an H₂ treatment at 1000 K, both samples still show W4f_{7/2} peaks that are attributed to W⁶⁺ and W⁵⁺ species with majority of species in the W⁵⁺ state for both samples, 77% for 6W-SiO₂ and 80% for 1Pd-6W-SiO₂, as shown in **Figure 3.5c**. The difference between the W4f_{7/2} peak positions of W⁶⁺ and W⁵⁺ species is 1.4 eV and 1.2 eV for 6W-SiO₂ and 1Pd-6W-SiO₂, respectively. As the W4f_{7/2} position of W⁴⁺ is expected to be 2.8-3.0 eV lower than that of W⁶⁺, ^{20,21} we found no evidence for W⁴⁺ in our samples even after treatment in H₂ up to 1000 K. Instead, the final oxidation state of W on these samples after reduction treatment is primarily +5, with some species still in the +6 oxidation state.

Work done on comparable systems such as unsupported Pd-MoO₃ catalysts, has shown unpromoted molybdenum oxide resides in a primarily +6 oxidation state, even under reducing conditions up to 673 K, while the addition of Pd allows for reduction to +5 and +4 Mo species.⁴⁰ While our SiO₂-supported tungsten species exist in a +6 and +5 oxidation state, similar to what has been previously reported for un-supported Pd-WO_x catalysts,⁴³ the addition of Pd helps facilitate the reduction of the tungsten oxide to a higher fraction of +5 species, especially at temperatures of or below 800 K.



Figure 3.5: In situ photoemission spectra and peak fits of the W4f region for 6W-SiO₂ and 1Pd-6W-SiO₂ samples following a treatment in 5%H₂/N₂ at 30cm³ min⁻¹ at **a**) 600 K, **b**) 800 K and **c**) 1000 K. Percent of W⁶⁺ and W⁵⁺ speciation was calculated based on the area of their respective W4f_{7/2} peaks. Spectra were charge referenced to the Si 2p peak at 103.5 eV.

To elucidate the oxidation state changes of WO_x species supported on P25-TiO₂ the same procedure was followed. The spectra were charge referenced to the Ti $2p_{3/2}$ peak at 458.7 eV as that peak showed no change in shape, i.e., broadening, Figure B11, which suggests most of the Ti cations in the support analyzed by XPS remained as Ti⁴⁺ following thermal treatments in H₂. Thus, the Ti 3p peaks of the titania support were assumed to be constant during fitting of WO_x peaks (based on fitting of the bare P25-TiO₂ support after the same reducing treatment as depicted in Figure B12). Consistent with SiO₂-supported samples, Pd was completely reduced to Pd⁰ after heating to 600 K in H₂ (Figure B14). Figures 3.6a-c show the W 4f (and Ti 3p) region of 6W-P25-TiO₂ and 1Pd-6W-TiO₂ samples following reducing treatments in 5% H₂/N₂ at 600, 800 and 1000 K respectively. Some tungsten oxide in a +5 oxidation was observed following reducing treatments at those temperatures on both samples, as well as the as-synthesized (non-reduced) sample (Figure **B13**) but overlap of the Ti $3p_{3/2}$ peak from the titania support prevented quantification of W in the +6 oxidation state relative to +5. Moreover, the broad nature of W 4d peaks also prevent quantification on our samples. Prior reports on Pt-W-TiO₂ catalysts have indicated that W exists primarily as +6, and that following H_2 reduction can further reduce to +5, while maintaining a larger fraction of the +6 oxidation state, albeit at higher H₂ partial pressures (> 0.1MPa).⁴ Importantly, the fraction of tungsten +5 determined by in situ XPS of our titania-supported samples does not change significantly during reducing treatments up to 1000 K regardless of the presence of Pd, which is in stark contrast to the SiO₂-supported species.



Figure 3.6: In situ photoemission spectra and peak fits of the W4f (and Ti 3p) region for 6W-P25-TiO₂ and 1Pd-6W-P25-TiO₂ samples following a treatment in 5% H_2/N_2 at 30cm³ min⁻¹ at **a**) 600 K, **b**) 800 K, and **c**) 1000 K. Spectra were charge referenced to the Ti 2p_{3/2} peak at 458.7 eV.

3.3.2.3 In situ X-ray Absorption Spectroscopy. To further explore the apparent difference in WO_x reducibility on the two supports, samples were monitored by X-ray absorption spectroscopy throughout a H₂-TPR experiment. Temperature limitations of the cell design limited the maximum temperature during TPR to 773 K, which is lower than that in the XPS experiments. **Figure 3.7** shows a comparison of the X-ray absorption near-edge structure (XANES) at the L_{III} edge of W before TPR, at 773 K, and after TPR. **Figure 3.7a** shows the edge energy for the 1Pd-6W-SiO₂ sample shifts from 10208.8 to 10208.2 eV, consistent with a change in oxidation state from W⁶⁺ to a lower oxidation state that is not reduced all the way to W⁴⁺ observed for WO₂ (**Figure B17**).



Figure 3.7: In situ XANES spectra of the W L_{III} edge before and after a TPR at 773 K under a flow of 5% H_2/N_2 at 20 cm³ min⁻¹ of **a**) 1Pd-6W-SiO₂ and **b**) 1Pd-6W-P25-TiO₂ with insets shown for clarity. Note: 1Pd-6W-SiO₂ data were collected in transmission mode and 1Pd-6W-P25-TiO₂ data were collected in fluorescence mode. See **Section 3.2.2** for more detail.

Upon cooling down the sample to room temperature in dihydrogen, the edge remained shifted, which indicates the sample remained reduced. **Figure 3.7b** shows the same TPR experiment on 1Pd-6W-P25-TiO₂, which had a small edge shift from 10208.7 eV to 10208.5 eV, and 10208.6 eV

at TPR conditions and upon cooling, respectively. The small change in the edge position (0.2 eV) during TPR indicates the tungsten oxidation state remained the same throughout the experiment, in agreement with the in situ XPS results.

Figures B18 and **B19** show the analogous two samples without Pd, $6W-SiO_2$ and $6W-P25-TiO_2$, did not incur a significant shift in the edge position during TPR (~0.2 eV). Indeed, for $6W-SiO_2$, there is very little reduction of WO_x below 773 K as illustrated by the TPR profiles in **Figure 3.4a**. The edge position of the Pd-free samples corresponded to a W oxidation state of around +6 for tungsten oxide on SiO₂ and TiO₂, respectively.

The results from the in situ XANES of the SiO₂-supported samples agree with the in situ XPS results, in which Pd aids in reducing the tungsten oxide species from majority +6 to mostly +5 species. However, while the XAS results suggest an oxidation state of near +6 for all the TiO₂-supported samples regardless of reduction temperature and presence of Pd, the XPS shows the presence of some W in a +5 state (**Figure 3.6**). This is likely due to the difficulty of XPS peak fitting, stemming from the overlap of the Ti 3p regions of the P25-TiO₂ support on both 1Pd-6W-P25-TiO₂ and 6W-P25-TiO₂. Regardless, the observed trends from in situ XANES and XPS show significant changes in W oxidation state during TPR of 1Pd-6W-SiO₂ but negligible changes in W oxidation state during TPR than their bare supports (**Figure B6**), the fact that W reduces when supported on SiO₂ and remains in the same oxidation state on TiO₂ is intriguing. Therefore, we used molecular modeling to rationalize these disparate outcomes for the two supports.

3.3.3 Computational Modeling of Supported WO_x **Clusters.** To investigate the differences in W reducibility observed in the experiments, we used hybrid density functional theory calculations (HSE06 functional, full details in **Section 3.2.3**) to model the molecular and electronic structures of variable stoichiometry tungsten oxide clusters on the two supports. Results for WO_x clusters supported on TiO₂ are reported in **Section 3.3.3.2**, and we begin here with SiO₂.

3.3.3.1 SiO₂-supported WO_x. We used the β -crystabolite-SiO₂ (001) surface as a surrogate model for amorphous silica that preserves its electronic properties while avoiding the configurational sampling issues inherent to amorphous supports (additional discussion and validation provided in Section 3.2.3 and Figure B29). Notably, the (001) surface displays a density and refractive index similar to amorphous silica and can be hydroxylated to generate a silanol density comparable to that of amorphous silica.⁴⁴⁻⁴⁶ Figure B29 demonstrates that phase diagrams generated for a W monomer on the β -crystabolite-SiO₂ (001) surface remain similar in relative energy and structure to the monomer supported on amorphous silica. To represent different size tungsten oxide clusters, we used W monomers, dimers, and trimers. Grafting these clusters on the SiO₂ surface (terminated with silanol groups) requires the removal of at least one surface H atom, enabling W to bind with one or more undercoordinated surface O atoms. We generated configurations removing between 1 and 4 H atoms from the top of the SiO₂ slab and attaching W to the surface O atom(s). Details of the structure generation and the different configurations considered are described in Section B.2.

Comparing the free energy of these structures under conditions relevant to catalyst synthesis across different temperatures (**Figure B30a**, 0.01 kPa H₂O, 20 kPa O₂, 300 to 1000 K, since catalyst synthesis undergoes thermal treatment at 923 K), W₃ structures (trimers) are more stable than W monomers and dimers from 300 to 1000 K. This result is consistent with the higher population of larger W aggregates relative to highly dispersed W observed using STEM following impregnation

and treatment in flowing dry air at 923 K. To explore how different W clusters evolve under exposure to H₂, we chose the lowest free energy structures under synthesis conditions at 923K, **Figures B21, B23,** and **B25.** For the dimer and trimer configurations, there are two structures within a 50 kJ mol⁻¹ range at 923 K, so we considered both as starting structures.

Figure 3.8 reports the starting structure for different W domain sizes using the nomenclature $(SiO_2)H_a - W_bO_c$. For example, in the W monomer species $(SiO_2)H_6 - WO_2$, $(SiO_2)H_6$ indicates 6 remaining H atoms on the silica surface (with 2 H atoms removed for monomer grafting), and in this example WO₂ signifies the addition of 1 W and 2 O atoms to establish the initial structure for the W monomer.

Palladium-catalyzed dissociation of H_2 to 2H creates a reservoir of H atoms that can transport via spillover and may react with tungsten oxide clusters. Two different reactions for reduced W species in each cluster size were considered – H attached to an O atom in the grafted tungsten oxide cluster (forming a Brønsted acid site, green shading) and dehydration with tungsten oxide forming an open coordination site (a Lewis acid site, blue shading). We considered a cascade of adding H and removing O atoms, including all intermediate combinations. The reaction cascade was terminated when: consecutive H addition energies were endothermic, or the O removal energy is greater than 70 kJ mol⁻¹. We considered all possibilities (removal of each O and H addition to each possible O) for each reaction, and **Figure 3.8** reports the lowest energy pathway for the reaction considered.



Energies in kJ/mol

Figure 3.8: Reaction energies for different speciation of silica supported W clusters. Green shaded structures were generated from H-addition, and blue shaded structures from O-removal. Schematic representations for the structures are shown on the left. Molecular structures are provided as supplementary materials.

Figure 3.9 shows T-P_{H2} phase diagrams generated using the library of structures generated in **Figure 3.8**. **Figure 3.9** shows that only one tungsten oxide monomer species, $(SiO_2)H_6 - WO_2$, is lowest in free energy across a wide range of conditions among all monomer structures considered. The $(SiO_2)H_6 - WO_2$ structure is fourfold coordinated to oxygen in a tetrahedral configuration, similar to tetrahedral and distorted tetrahedral configurations reported for other oxide supported tungsten monomers.^{17, 30, 47-49} Starting from $(SiO_2)H_6 - WO_2$, it is thermodynamically unfavorable (Figure 3.8) to either add H to an O or remove O. Oxygen removal disrupts the tetrahedral configuration to a trigonal planar configuration, which is not a stable coordination environment for W. As the W domain size increases, a broader array of tetrahedral coordination options becomes available for the tungsten oxide clusters. Figure 3.9 also shows the three most stable W dimer species across a wide variety of conditions, and two of these have tetrahedrally coordinated W atoms.



Figure 3.9: Ab initio thermodynamic phase diagrams for silica supported WO₃ monomer, dimer, and trimer at $P_{H2O} = 0.01$ kPa, where P^o is the reference pressure of 101.3 kPa. Gray boxes report the oxidation state of W. Generated using HSE06.

Figure 3.9 shows Bader charge analysis results for structures in the phase diagram, revealing a reduction in W oxidation state with increasing temperature for W dimers and trimers. Consistent with the Bader charge analysis, integration of the HSE06 computed DOS (**Section B.4.2**) shows a significant increase ($\geq 1 e^{-}$) in the number of occupied states (total e^{-}) for the W dimer and trimer species that form at high T and P_{H2} relative to the species that form at low T. The reduction of the W species in the larger tungsten oxide domain sizes is consistent with the in situ XPS results shown in **Figure 3.4** that showed an increase in the amount of the W⁵⁺ species with an increase in temperature.

3.3.3.2 TiO₂-supported WO_x. To compare differences in W reducibility between a nonreducible support (SiO₂) and a reducible support (TiO₂) we used a similar workflow to Section 3.3.3.1 for variable stoichiometry tungsten oxide clusters supported on titania. Titania exists in three phases: anatase, rutile and brookite.⁵⁰ We used anatase (space group: *I41/amd*) and rutile, (space group: P42/mnm) as the P-25 TiO₂ support used to synthesize the samples is a mixture of both rutile and anatase TiO₂ (Figure B15 and Table B13). We started with the most stable surface of both polymorphs, which are the (110) surface of rutile,⁵¹ and the (101) surface of anatase.⁵² Similar to the silica-supported materials, we generated initial W clusters (monomers, dimers, and trimers) where all W atoms exhibit formal oxidation states of $+5^{16}$ or +6, and used a Basin-Hopping optimization scheme, described in Section 3.2.4, to find the lowest energy configurations. Multiple initial guesses for the W clusters on the anatase and rutile support converged to the same final lowest energy structure. These structures were used as the starting structures for the H addition and O removal reactions. Figure B31a shows that under synthesis conditions (923 K, 0.01 kPa H₂O, 20 kPa O₂), the anatase-supported W clusters prefer to form monomers whereas dimers are preferred on the rutile support. The preference to form monomers and dimers on titania is consistent with the dispersed WO_x clusters seen in the STEM images (Figure 3.3).

Figure 3.10 reports the most exothermic energies for the reaction energies considered in the cascade of adding H and removing O atoms. Analogous to the procedure used with SiO₂, the reaction cascade was terminated when: consecutive H addition energies were endothermic, or O removal energies were greater than +70 kJ mol⁻¹. The reaction energy for H addition to most of the W clusters supported on both anatase and rutile titania is exothermic, in contrast to H addition for the SiO₂ support (**Figure 3.8**), suggesting that addition of H to the W cluster is more favorable when the support is reducible.

WO₃ on rutile TiO₂



WO₃ on anatase TiO₂ $WO_3 \xrightarrow{-8} WO_3H$ 14 WO_3H_2 0 139 $WO_2 \xrightarrow{4} WO_2H$ <u>18</u> WO₂H₂ 0 0 w 104 WO Ti Ti 0 $\xrightarrow{15} W_2O_6H_2$ $\xrightarrow{-54}$ W₂O₆H W₂O₆ 24 W₂O₅ _-9 27 → W₂O₅H₂ W₂O₅H C 130 W_2O_4 Ó Ô Ťi W₃O₉

b)



Energies in kJ/mol

Figure 3.10: Reaction energies for different speciation of a) rutile and b) anatase supported W clusters.

Figure 3.11 reports the thermodynamic phase diagrams constructed using the library of structures from Figure 3.10. The speciation of the W clusters changes with the temperature and pressure conditions and depends on the cluster size. Oxygen vacancies are generated at higher temperatures and pressures, whereas Brønsted acid sites are generated at lower temperatures (<600 K). The phase diagrams for W supported on titania in Figure 3.11 include W species with H added, which was not noted for the silica support (Figure 3.9). Hence, W clusters supported on titania are more likely to form Brønsted acid sites than W supported on silica. In 5% H₂ (the in situ XPS reducing treatment), the oxidation state of W across the different species does not change significantly on either titania support. Most species featured on the phase diagram for titania-supported WO₃ clusters exhibit a tetrahedral configuration, consistent with the stable configurations on silica. Previous reports have indicated that W prefers to be highly dispersed and form tetrahedral monomeric species on alumina, titania and ceria supports.^{17, 47, 48, 53-55} However, the monomer supported on rutile exhibits a square pyramidal geometry with five-fold coordination. While this phenomenon has been reported before,⁴⁹ it is not as commonly observed as the tetrahedral configuration, which is more prevalent in the case of monomer supported on anatase. For monomers supported on anatase, all the thermodynamically stable species depicted in the phase diagram exhibit a tetrahedral configuration. The tetrahedral coordination is also adopted by the dimers on both anatase and rutile. For the dimer supported on rutile, the configuration with one oxygen vacancy is formed preferentially over the starting structure. Both structures are tetrahedrally coordinated, but the structure with the 1O vacancy forms a tetrahedral configuration with a surface oxygen atom, thereby generating increased stability.

The DOS analyses from HSE06 calculations (Section B.4.3 and B.4.4) demonstrate little to no variation in the integrated total Density of States (DOS) for W among different species. This
observation is consistent with the in situ XPS (and in situ XANES up to 773 K) of the titaniasupported samples, which indicated that increasing the temperature of reduction did not change the oxidation state of W. In contrast to the behavior of W on titania, a previous report in literature⁵⁶ has shown that the Mo atom on the molybdenum oxide monomers and dimers supported on anatase are reduced from Mo^{6+} to Mo^{5+} . Likewise, experimental and computational results in our work with the silica support showed that the W reduces from +6 to +5.



Figure 3.11: a) Ab initio thermodynamic phase diagram for rutile TiO_2 supported WO₃ monomer, dimer, and trimer. **b)** Ab initio thermodynamic phase diagram for anatase TiO_2 supported WO₃ monomer, dimer, and trimer. Gray boxes report the oxidation state of W. Generated using HSE06.

Several studies have indicated that for the range of conditions that we consider for the phase diagrams, there may be oxygen vacancies on the titania surface.⁵⁷⁻⁶¹ To explore the effect of the surface oxygen vacancies on the relative stability of the WO₃ clusters, we generated O vacancies

in the proximity of the W clusters and subsequently recomputed the phase diagrams, reported in (Section B.3.1). Only O atoms that are not directly bonded to the W cluster are removed to generate the vacancy. In general, we found only a slight increase in stabilization of the initial WO₃ cluster. Notably, the oxidation state of W in the WO₃ clusters did not vary significantly with the presence of an oxygen vacancy on the surface.

Summarizing, the support composition affects the trends in the reduction of tungsten oxidation states with increasing temperature. The larger W clusters on silica are reduced with an increase in temperature, whereas the W clusters supported on titania did not show a significant change in W oxidation state. The W clusters on both supports show similar trends in W configurations. Tetrahedral W configurations are the predominant species on both supports, reflecting the preference for W to coordinate tetrahedrally in oxidation states of +5 and +6.

We also combined structures with different cluster sizes on a given support into one model (**Figure B30b** and **B31b**) and evaluated the thermodynamic behavior at acid conditions relevant to carboxylic acid reduction (423 K, 0.01 kPa H₂O and 5 kPa H₂).⁵ At these conditions, the W supported on both anatase and rutile titania preferentially form monomers with one Brønsted acid site, whereas the silica-supported catalysts favor the formation of Brønsted acid sites on the trimer. Conversely, Lewis acid sites (open coordination sites on W) are not thermodynamically favorable under any relevant conditions. Taken together, the analysis shows that under various relevant catalytic conditions in the presence of H₂, Brønsted acid sites would be expected to contribute as active sites, as suggested by Wu et al. and He et al.^{4,7}

3.3.4 Charge Density Comparison for SiO₂ and TiO₂-supported WO₃. The results from the in situ XPS and XAS experiments on the SiO₂ supported Pd-W samples indicate the W reduces from a +6 oxidation state to primarily +5 during TPR. Interestingly, while the TPR profiles of TiO₂ supported samples (**Figure 3.6**) suggested there was hydrogen uptake from both 1Pd-6W-P25-TiO₂ and 6W-P25-TiO₂, the tungsten oxide species did not show a change in oxidation state in both XPS and XAS.

To elucidate the difference in the W oxidation state between the two supports, we computed the charge densities of the surface atoms for the different supports. Figure 3.12 shows the charge differences on the W clusters and surface atoms with the addition of 1H on the silica and anatase titania supports. The charge difference for O removal for the WO_x species on all the supports tested is reported in Section B.5. For the silica-supported W clusters, the redistribution of charge with the addition of 1H atom is largely localized to the W atom(s), in agreement with the change in oxidation state seen in the W in the experimental and computational results. For the W monomer on silica, a significant charge difference is also seen on the O atom attached to the W to which the H is added. In contrast, the additional charge for the titania-supported cluster is mostly distributed among the surface Ti and O atoms, in agreement with literature reports that indicate delocalization of charge across multiple surface Ti atoms.^{62, 63} Similarly, for W dimers and trimers supported on silica, the charge from the additional H atom is largely localized on the W and the bridging O atoms. The W trimer supported on anatase titania has a larger charge difference on one of the W atoms; however, it is still lower than the overall charge differences for W on silica. Across all cluster sizes, there is little difference in the charge density of the different cluster sizes of W atom supported on anatase and rutile titania, which supports the lack of significant change in the oxidation state of W in the titania supported clusters.



Figure 3.12: Differences in charge density of surface atoms on silica, anatase and rutile titania supports for H addition reaction for **a**) monomer **b**) dimer and **c**) trimer. In the inset molecular figure, truncated after the first support layer, the filled circle around the atoms indicates the absolute charge difference after H addition. The radius of the circle is proportional to the change in absolute charge for the individual structures. The molecular figure indicates how the charge is localized and is not a scale representation of the bar graph.

Figure 3.13 shows a correlation of the the direct bandgap associated with the tungsten oxide cluster (which is inversely related to cluster size) to the hydrogen consumption during TPR up to 1223 K. The 2W-AT-SiO₂ sample showed the highest bandgap, (smallest oxide cluster size) and the lowest H₂ consumption per mol W, consistent with its high stability. Lower band gap materials (larger cluster sizes) consumed more H₂ during TPR, and the bulk WO₃ sample consumed the most H₂, equivalent to nearly complete reduction to metal. While this result is only on the SiO₂ supported samples and bulk WO₃ (due to the overlap of TiO₂ band in DR UV-Vis, **Figure B3**) experimentally, it shows larger tungsten oxide clusters consume more H₂, and are thus more likely to reduce, in agreement with the computational observations in **Section 3.3.3.1**.



Figure 3.13: Correlation of H_2 consumption per mol W, calculated from H_2 -TPR results, versus the direct bandgap of WO_x species, calculated from DR UV-Vis.

3.4 Conclusions

The synthesis and reducibility of supported tungsten oxide clusters are influenced by several factors. Silica-supported tungsten oxide clusters prepared by incipient wetness impregnation form primarily 1-3 nm sized clusters but could be made smaller by acid-treating the silica and utilizing a lower loading of W. Titania-supported tungsten oxide clusters are highly dispersed and subnanometer in size on P25-TiO₂. Results from H₂-TPR show addition of Pd on W-SiO₂ aids in the reduction of WO_x by decreasing its initial reduction temperature, suggesting a significant influence of hydrogen spillover associated with Pd, whereas TiO₂-supported W showed little difference in initial reduction temperature with added Pd. The hydrogen spillover associated with the Pd aided in the reduction of W in SiO₂-supported tungsten oxide species from a +6-oxidation state to a mixture of +6 and +5 at 600 K. At higher reduction temperatures (up to 1000 K), W on silica was primarily in the +5 oxidation state regardless of Pd promotion. In comparison, the W in TiO₂supported WO_x species did not appreciably change oxidation state, even with the addition of Pd. Charge analysis of TiO₂-supported model clusters revealed charge delocalization across the titania support during reduction, which accounts for the lack of W oxidation state change during reduction treatments. On both supports, WO_x clusters prefer to remain in a tetrahedral configuration regardless of the reduction state. At temperatures and H₂ partial pressures relevant to catalysis, results from model clusters on silica and titania reveal that Brønsted acid sites are likely to be present, as undercoordinated W atoms (potential Lewis acid sites) are thermodynamically unfavorable.

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Chapter 4: Reduction of Propionic Acid to Propanol over Pd-Promoted WO_x Supported on SiO₂ and TiO₂

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Abstract

Platinum group metal (PGM) promoted reducible metal oxides are known to be active catalysts for the reduction of carboxylic acids to their corresponding aldehydes and alcohols. In this work, the reduction of propionic acid to propanal and propanol was used as a model system to investigate the effect of support on the performance of Pd-promoted tungsten oxide catalysts. Silica and titania supported Pd-W catalysts were synthesized via wetness impregnation and were evaluated via the gas-phase reduction of propionic acid with H_2 . High resolution STEM imaging confirmed the presence of nm-size Pd particles on both Pd-W-SiO₂ and Pd-W-P25-TiO₂ catalysts. During the steady state conversion of propanoic acid, the presence of Pd on both W-SiO₂ and W-P25-TiO₂ enhanced the selectivity and formation rate of reduction products propanal and propanol, with a combined selectivity of >96% at a conversion of 1 % for Pd-W-SiO₂ and 9.2% for Pd-W-P25- TiO_2 catalysts. In the presence of the P25-TiO₂ supported Pd-W catalyst, the reaction order in H₂ was 0.3 and the order in propionic acid was nearly zero, while the apparent activation energy of the reaction was 64 kJ mol⁻¹. Although increasing the Pd loading on P25-TiO₂-supported W catalysts increased the combined propanal and propanol formation rate, additional Pd had a marginal influence on the SiO₂-supported W catalysts. Most importantly, the P25-TiO₂-supported Pd-W catalysts exhibited order of magnitude higher formation rates of propanal and propanol compared to the SiO_2 analogs.

4.1 Introduction

The catalytic conversion of biomass into higher-value products has garnered significant attention recently. Selective hydrodeoxygenation (reduction) of bio-derived carboxylic acids is of particular interest because the formed aldehydes and alcohols can be further utilized in the production of plasticizers, detergents, and lubricants.^{1, 2}

Reducible metal oxides such as ReO_x, MoO_x, and WO_x have demonstrated catalytic activity in the reduction of carboxylic acids when promoted with a platinum group metal (PGM) such as Pd or Pt.^{1,3-11} For example, Pd-ReO_x-SiO₂ catalyzed the liquid phase hydrodeoxygenation of stearic acid with H₂ to stearyl alcohol with a 97% selectivity across a conversion range of 8 % to 33 %.⁷ Kammert *et al.* reported 81% selectivity to 1-propanol at 7% conversion of gas phase reduction of propionic acid with H₂ over a Pd-ReO_x-SiO₂ catalyst. An analogous TiO₂-supported Pd-ReO_x catalyst had 84% selectivity to 1-propanol at 8% conversion under similar conditions.¹² Due to the high cost and volatile nature of Re oxides, both MoO_x and WO_x have attracted more interest recently as components of hydrodeoxygenation catalysts.

Gomez *et al.* showed that the addition of Pt, at a weight loading of only 0.05%, on MoO₃ increases the rate of selective hydrodeoxygenation of pentanoic acid compared to bare MoO₃ and lowers the apparent activation barrier for acid conversion by 32 kJ mol⁻¹. Addition of a small amount of Pt also facilitated a significant reduction of Mo⁶⁺ in the oxide to Mo⁵⁺ and Mo⁴⁺ species when exposed to H₂, as revealed by X-ray photoelectron spectroscopy (XPS).³ They suggest the reaction takes place on oxygen vacancies of the metal oxide surface that are generated by a supply of H atoms originating via spillover from the Pt promotor.¹¹ Studies by Albarracin-Suazo *et al.* and Nancy *et al.* for hydrodeoxygenation chemistries also confirmed via XPS that Pd promotion aids in the reduction of MoO_x species to primarily +5 when supported on TiO₂ where the partially reduced MoO_x centers, generated via hydrogen spillover, are thought to facilitate selective C-O bond cleavage.^{13, 14} Kammert *et al.* showed Pd-WO_x-SiO₂ and Pd-WO_x-TiO₂ catalyze reduction of propionic acid by H₂ with a selectivity to 1-propanol >80% at relatively low conversions (<15%).⁵ While there is general agreement regarding the activity and selectivity of these PGM-promoted reducible metal oxides in the reduction of carboxylic acids, the nature of the active sites is still under debate. Conversion of carboxylic acids to their corresponding alcohols occurs in a multistep sequence in which formation of an aldehyde intermediate is the kinetically limiting step that occurs on the reducible metal oxide and subsequent hydrogenation of the aldehyde to alcohol is rapid on the PGM.^{4, 12} Brønsted acid sites have been hypothesized to play a role by facilitating the dehydration step in the reduction of carboxylic acids to their corresponding aldehydes which further hydrogenates over the PGM.⁴ Furthermore, the spillover effect from PGM's has long been studied on reducible metal oxides¹⁵⁻¹⁷ and may contribute to the formation of Brønsted acid sites in the presence of H₂^{12, 18, 19}, thus leading to active catalysts for the reduction of carboxylic acids.

The influence of support type with the reducible metal oxides and PGM's in the case of hydrogen spillover has been a widely studied topic. For example Karim *et al.* recently showed that the migration of H atoms from Pt to FeO_x is able to occur over greater distances (up to 45 nm) and at a higher rate on a reducible support such as TiO₂ compared to an insulating support such as Al_2O_3 .²⁰ Thus, in the case of spillover, TiO₂ has been shown to be a better support. Our recent work expanded on the influence of support on tungsten oxide reducibility and showed that WO_x species are more reducible on SiO₂ than on TiO₂. In Chapter 3 it was demonstrated that when promoted with Pd in an H₂ environment, SiO₂ supported tungsten oxide is able to reduce from a +6 oxidation state to primarily +5. However, when supported on TiO₂, the primary fraction of +5 tungsten oxide remains unchanged even in the presence of Pd.

While Pd-promoted WO_x catalysts on both supports, SiO₂ and TiO₂, are active catalysts in the reduction of carboxylic acids,⁵ it is not clear how the support affects tungsten oxide performance in the reaction. Past research generally regards hydrogen spillover as a mechanism to generate Brønsted acid sites on the reducible metal oxide^{18, 21, 22}, which have been suggested as the active site in the conversion of propionic acid to 1-propanol.⁴ Hydrogen spillover has been shown to be more extensive on the TiO₂ support,^{20, 23} however the reducibility of the active tungsten oxide is more prominent on SiO₂, as was shown in Chapter 3. Given the clearly different nature of WO_x clusters on SiO₂ and TiO₂ in a reducing environment, we aim to examine the influence of the support on the catalytic performance of the supported WO_x in the reduction of propionic acid to propanol.

4.2 Methods

4.2.1 Catalyst Synthesis. High-purity SiO₂ (Sigma-Aldrich, Davisil 635, 60 Å, 480 m² ·g⁻¹, 150-250 μ m) was used for the SiO₂-supported catalysts. For W-SiO₂ catalysts, a desired amount of ammonium metatungstate (Aldrich, 99.99%) was mixed with distilled, deionized (DDI) water to achieve a solution that was equal to the pore volume of the silica support, which was then added dropwise onto the support until the point of incipient wetness. Samples were dried overnight in air at room temperature, followed by a 2 h in air at 393 K, and thermally treated at 923 K in 100 cm³ min⁻¹ flowing air (Praxair) for 4 h. For Pd-W-SiO₂ catalysts, the same incipient wetness impregnation (IWI) procedure was followed using tetraaminepalladium(II) nitrate solution (10 wt% in H₂O, Sigma-Aldrich) as the precursor and the already synthesized W-SiO₂, followed by the same thermal treatments as described above.

Titania-supported catalysts were also prepared using the same IWI procedure and thermal treatments as the SiO₂-supported catalysts. Mixed phase P25-TiO₂ (Sigma-Aldrich, P25

nanopowder, 21 nm), and rutile-TiO₂ (R-TiO₂) (Sigma-Aldrich, nanopowder, <100 nm, 99.5%) were used as the TiO₂ supports.

4.2.2 Catalyst Characterization. X-ray fluorescence (XRF) measurements were performed by Horiba Scientific (Piscataway, NJ) with an XGT-9000 XRF analytical microscope equipped with a 50W Rh anode X-ray tube. Spectra were collected in a partial vacuum over an area of 12.5 mm², an energy resolution of less than 143 eV at Mn-K α , and an accelerated voltage of 50 keV. Component concentrations were calculated using the Fundamental Parameters Method.

High resolution high-angle annular dark field (HAADF) scanning transmission electron microscope (STEM) images were recorded on a Thermo Fisher Scientific Themis Titan 3591 STEM operating at 200 kV and equipped with a monochromator and probe correction. The STEM-HAADF detector (Fischione) collection angle was set to 50-200 mrad at 115 mm camera length. Samples were either slurried in ethanol first or directly deposited on lacey or holey carbon films supported on copper grids.

Dihydrogen chemisorption experiments were performed on a Micromeritics ASAP 2020 Plus instrument. Prior to analysis, samples were treated in flowing H₂ at 473 K for 2 h, evacuated and cooled to 373 K for analysis. The temperature of 373 K was selected to prevent formation of b-phase Pd hydride during the chemisorption experiment. Dihydrogen was then dosed from 0.001 to 0.06 MPa. The H₂ uptake was determined by extrapolating the linear part of the high-pressure region of the isotherm to the zero pressure.

4.2.3 Catalytic Reactions of Propionic Acid. The sequential reaction of propionic acid to propanal and 1-propanol was carried out in a continuous downflow fixed bed stainless steel reactor tube (I.D of 0.46 cm) near 1 atm total pressure. A thermocouple inserted through the top of the

reactor was in contact with the catalyst. Catalysts were heating to 673 K in flowing N_2 (Linde, NI 5.0 UH-T) at a rate of 10 K min⁻¹ and held for 1 h, after which the reactor was cooled down to the desired reaction temperature.

Propionic acid (Sigma-Aldrich, \geq 99.5%) was supplied via a stainless-steel vapor saturator maintained at a constant temperature. Reaction kinetics were studied by varying the partial pressures of propionic acid (1.3-2.6 kPa), H₂ (0-0.1 MPa) in a balance of N₂ over a temperature range of 413 to 433 K. Propanal and propanol rate of formation over Pd-W-SiO₂ catalyst was relatively unchanged when amount of catalyst was changed (**Figure C9**).

Reaction products were analyzed by an on-line Agilent 7890A GC equipped with an MXT-WAX (ID of 0.53mm, 1 μ m film thickness, 30 m) column and a flame ionization detector. Methane (Praxiar, 99.97%) was added downstream of the reactor prior to entering the GC as an internal standard for measurement for rates. When product selectivities were desired, the methane was not added to the exit stream as it would interfere with quantification of light hydrocarbons (calculated on a C₃ basis), if any, and because they could not be separated on the column that was optimized for oxygenates. Propionic acid conversion and product selectivity were calculated based on **Eqs 4.1 and 4.2**, respectively, where n_i is the number of carbon atoms in product *i*, M_i is the effluent molar flow rate of carbon product *i* and M_a is the effluent molar flow rate of unreacted propionic acid.

conversion (%) =
$$\frac{\sum n_i M_i}{3M_a + \sum n_i M_i}$$
 Eq 4.1
selectivity_i (C%) = $\frac{n_i M_i}{\sum n_i M_i}$ Eq 4.2

4.3 Results and Discussion

4.3.1 X-ray Fluorescence, H₂ Chemisorption, and Microscopy. Elemental analyses via XRF are presented in **Table 4.1**. Chemisorption of H₂ on the 0.2Pd-6W-SiO₂ catalyst yielded a result of 54 % Pd metal exposed which would suggest about 2 nm size Pd particles. High resolution-STEM images of the 0.5Pd-6W-SiO₂ catalyst in **Figure 4.1** show particles in the range of 2-5 nm, which is fairly consistent with the estimated Pd size on a lower loaded sample (0.2Pd-6W-SiO₂) determined from H₂ chemisorption. The micrograph in **Figure 4.2** shows highly dispersed tungsten oxide clusters on the 0.5Pd-6W-P25-TiO₂ catalyst, while **Figure 4.3** shows a Pd nanoparticle, on the order of 5-10 nm, on the same catalyst. While both supports show Pd particles in the nanometer size range, there appears to be a larger number present on the SiO₂ support.

Sample	XRF Composition (wt%)		
	Pd	W	
6W-SiO ₂		5.6	
6W-P25-TiO ₂		5.7	
0.5Pd-SiO ₂	0.4		
$0.2Pd-6W-SiO_2$	0.2	5.2	
$0.5Pd-6W-SiO_2$	0.6	5.5	
$1Pd-6W-SiO_2$	1.1	5.9	
0.5Pd-TiO ₂	0.4		
0.1Pd-6W-P25-TiO ₂	0.1	5.6	
0.2Pd-6W-P25-TiO ₂	0.2	5.9	
0.2Pd-6W-R-TiO ₂	0.2	5.2	
0.5Pd-6W-P25-TiO ₂	0.5	5.8	
1Pd-6W-P25-TiO ₂	1.1	5.7	

Table 4.1: Elemental analysis of Pd, W, and Pd-W SiO₂- and TiO₂-supported catalysts determined via XRF



Figure 4.1: High resolution HAADF-STEM images of 0.5Pd-6W-SiO₂ catalyst with elemental mapping for Pd, W, and Si over the same region.



Figure 4.2: High resolution HAADF-STEM image of 0.5Pd-6W-P25-TiO₂ catalyst.



Figure 4.3: High resolution HAADF-STEM images of $0.5Pd-6W-P25-TiO_2$ catalyst with elemental mapping for Pd, W, and Ti over the same region.

4.3.2 Conversion and Product Selectivity of SiO₂- and TiO₂-supported Pd, W, and Pd-W Catalysts. The conversion of propionic acid, product distribution, and formation rate of propanal and propanol in mol s⁻¹ observed during reaction over the various catalysts are presented in Table **4.2**. It should be noted that the temperature and gas flow rates were the same in all of the experiments. As physical mixtures of various components of the catalysts were tested, there was no straightforward normalization method for the rate, so the catalyst masses are included in the Table to help interpret the results from the physical mixture experiments. The propionic acid conversion levels varied from 0 to 9.2 % conversion, depending on the catalyst. The 0.5Pd-SiO₂

catalyst without any tungsten present showed high selectivity (76 %) to the light hydrocarbon (LHC) products while propanal and propanol made up the remaining 24 % selectivity. The 0.5Pd-P25-TiO₂ without any tungsten showed higher selectivity to propanol and propanal (91%) relative to its SiO₂-supported analogue without tungsten. Manyar et al. have previously showed TiO₂ is a reducible oxide that can potentially catalyze carboxylic acid reduction in the presence of added Pt.²⁴ The 6W-SiO₂ catalyst without any palladium present was not active in this reaction, although its TiO₂ supported analog did show selectivity to propanol. The formation rate over the 6W-P25- TiO_2 , however, was two to three orders of magnitude lower relative to the other P25-TiO₂ catalysts containing Pd and W. Physically mixing 0.5Pd-SiO₂ with 6W-SiO₂ slightly increased propionic acid conversion (0.9 %) and increased the selectivity to propanol (20 %) compared to the 0.5Pd-SiO₂ catalyst (0.2% and 4 %, respectively). A physical mixture of the 0.5Pd- and 6W-P25-TiO₂ components also showed a similar trend, with an increase in the acid conversion (2.9 %) and selectivity to propanal and propanol (96%) relative to both components separately. Since the 6W-P25-TiO₂ (without added Pd) was 71% selective to propanol, albeit at a low conversion (<0.1 %), a physical mixture of 0.5Pd-SiO₂ and 6W-P25-TiO₂ was tested. Interestingly, a higher selectivity and combined formation rate of propanal and propanol (69 % and 5.9 $\times 10^{-9}$ mol s⁻¹, respectively) compared to the SiO₂-supported physical mixture (44 % and 2.2 x10⁻⁹ mol s⁻¹) suggests the support may play an important role in the generation of active sites on the tungsten oxide. Compared with the physical mixture of separate SiO₂-supported W and Pd components, the co-impregnation of Pd and W onto the silica (0.5Pd-6W-SiO₂) produced a catalyst with substantially higher selectivity to propanol at 87 % at 1 % conversion. The co-impregnated 0.5Pd-6W-P25-TiO₂ catalyst had the highest rate of formation compared to all the catalysts in Table 4.2, with an equally high selectivity to propanal and propanol, at 97 %. The improved activity from co-impregnating Pd and W on

both supports, SiO₂ or P25-TiO₂, suggests the interaction between Pd and W is critical to the catalytic activity, which could be the result of hydrogen spillover from the Pd.

	_	Selectivity			Propanal + Propanol		
Catalyst	Conversion	LHC	DPE	Propanal	Propanol	Formation Rate $(x10^{-9})$ $(mol \cdot s^{-1})$	
$0.5Pd-SiO_2$ $(0.15g)$	0.2	76	0	20	4	0.4	
0.5Pd-P25-TiO ₂ (0.15g)	0.8	8	1	3	88	2.7	
6W-SiO ₂ (0.15g)	0	0	0	0	0	0	
$6W-P25-TiO_2$ (0.15g)	< 0.1	0	29	0	71	0.04	
$ \begin{array}{r} 0.5Pd-SiO_2 \\ (0.15g) \\ + \\ 6W-SiO_2 (0.15g) \end{array} $	0.9	56	0	24	20	2.2	
0.5Pd-P25-TiO ₂ (0.15g) + 6W-P25-TiO ₂ (0.15g)	2.9	4	0	3	93	9.5	
$\begin{array}{r} 0.5 \text{Pd-SiO}_2 \\ (0.15 \text{g}) \\ + \\ 6 \text{W-P25-TiO}_2 \\ (0.15 \text{g}) \end{array}$	1.8	31	0	15	54	5.9	
0.5Pd-6W-SiO ₂ (0.15g)	1	4	0	9	87	3.7	
0.5Pd-6W-P25- TiO ₂ (0.15g)	9.2	2	1	0	97	30	
+ represent a physical mixture of two components, 0.15 g of catalyst, 0.5 g of total catalyst for							

Table 4.2: Conversion and product distribution from propionic acid reduction over select Pd, W, and Pd-W SiO₂- and P25-TiO₂-supported catalysts

+ represent a physical mixture of two components, 0.15 g of catalyst, 0.3 g of total catalyst for physical mixtures (0.15 g of each component), catalysts pretreated in flowing N₂ at 673 K for 1 h, 423 K, 1 atm, 15 cm³min⁻¹ H₂, 1.6 kPa propionic acid, 2 h TOS)

4.3.3 Kinetics of Reduction of Propionic Acid to Propanal and Propanol over Pd-Promoted W on TiO₂. Reaction orders in H₂ and propionic acid as well as the apparent activation energy for propionic acid conversion to propanal and propanol were measured over the 0.5Pd-6W-P25-TiO₂ catalyst with the results shown in Figure 4.4. The reaction rates were normalized by the moles of W since the physical mixture experiments confirmed the critical role of W on catalyst performance and STEM imaging (Figure 4.2) revealed nearly every W is available at the surface. The reaction orders were zero and 0.3 in propionic acid and H₂, respectively. The reaction order in H₂ is similar to a previously reported value of 0.2, whereas the zero order in propionic acid is different for the same catalyst and reaction reported earlier with a value of 0.7.5 We suspect the higher partial pressures of acid used here saturated the active sites. The apparent activation energy of propanal and propanol formation was 64 kJ mol⁻¹, which agrees well with a previously reported value of 54 kJ mol^{-1.5} We attempted to evaluate the reaction kinetics over the analogous SiO₂-supported catalyst, however surface hydroxyls on the SiO₂ support can interact with the products of the reaction resulting in strongly held propoxy species as has been previously shown⁴ and discussed in further detail in Appendix C. Reaction transients observed after changing partial pressure or temperature were too long to reliably measure the kinetic parameters on the silica-supported catalysts.



Figure 4.4: Formation rate of propanal and propanol as a function of **a**) propionic acid pressure (433 K, 1 atm, 50 cm³ min⁻¹ H₂) **b**) H₂ pressure (433 K, 1 atm, 50 cm³min⁻¹ total flow of H₂ +N₂, 1.6 kPa propionic acid) and **c**) temperature (1 atm, 50 cm³min⁻¹ H₂, 1.6 kPa propionic acid) over 0.5Pd-6W-P25-TiO₂. (All reactions used 0.10 g of catalyst and catalysts were pretreated in flowing N₂ at 673 K for 1 h.)

4.3.4 Effect of Support on Propanal and Propanol Formation Rate. To understand the effect of Pd on propanal and propanol formation, a range of Pd loadings was tested on the 6W-SiO₂ and 6W-P25-TiO₂ catalysts. The conversion level and product selectivities are summarized in **Table 4.3.** All catalysts were highly selective to propanal and propanol (combined selectivity of >95 %) and conversions varied from 5.4 % to 12.2 % for the P25-TiO₂ support and 0.2 % to 1.1 % for the SiO₂ support. **Figure 4.5** shows that across an order of magnitude increase of Pd loading on the 6W-P25-TiO₂ catalyst, ranging from 0.1 to 1.1 wt % Pd, the formation rate of propanal and

propanol, normalized on a per mol W basis, increased by only about 40%. Moreover, the correlation of the Pd loading to the propanal and propanol formation rate in **Figure 4.5** does not extrapolate to zero on the y axis for, suggesting that a very small amount of Pd aids in the generation of active WO_x sites. While there is also a minor positive effect of Pd loading on the rate observed over the SiO₂-supported catalysts, it is clearly not as significant as that observed with the P25-TiO₂ catalyst, and the rate extrapolates to the origin with no Pd loaded onto silica.

and -F25-1102-supported catalysis									
Catalyst	Conversion -	Selectivity							
		LHC	DPE	Propanal	Propanol				
$0.2Pd-6W-SiO_2$	0.2	0	0	28	72				
$0.5Pd-6W-SiO_2$	1	4	0	9	87				
1Pd-6W-SiO ₂	1.1	4	0	6	90				
0.1Pd-6W-P25-TiO ₂	5.4	2	0	1	97				
0.2Pd-6W-P25-TiO ₂	8.7	2	1	0	97				
$0.2Pd-6W-R-TiO_2$	1.4	8	0	3	89				
0.5Pd-6W-P25-TiO ₂	9.2	2	1	0	97				
1Pd-6W-P25-TiO ₂	12.2	2	1	0	97				

Table 4.3: Conversion and product distribution from propionic acid reduction over Pd-W-SiO₂ and -P25-TiO₂-supported catalysts

0.15 g of catalyst, catalysts pretreated in flowing N₂ at 673 K for 1 h, 423 K, 1 atm, 15 cm³ min⁻¹ H₂, 1.6 kPa propionic acid, 2 h TOS

Comparison of the propionic acid conversion for Pd and W on different TiO₂ supports is included in **Table 4.3** and **Figure C2** in the Appendix. As previously mentioned, the P25-TiO₂ (primarily anatase, with the rest rutile, **Table B13**) supported Pd-W catalyst showed the highest reduction rate at 5.9×10^{-4} (mol propanal + propanol)·(mol W)⁻¹·(s)⁻¹, while that over the rutile (R-TiO₂) supported P-W catalyst was six times lower at 1.2×10^{-4} . Differences in catalytic activity between the two titania polymorphs (anatase and rutile) and P25 (a mixture of anatase and rutile) have been previously reported in a variety of different catalytic reactions, ^{25, 26} and may be attributed to the higher surface area of P25 (**Table C1**), electronic differences between the two phases²⁷, or a combination of these properties. Nevertheless, the SiO₂-supported catalysts showed an order of magnitude lower rate compared to the P25-TiO₂-supported catalysts, thereby showing that the type of support has a substantial effect on the activity of these catalysts, regardless of the Pd loading. The STEM images in **Figures 4.1 and 4.3** suggest the size and distribution of Pd nanoparticles does not play a vital role in this activity difference between the P25-TiO₂ and SiO₂ supports. Instead, this may be due to the strong interaction between WO_x species and the P25-TiO₂ support as was shown in Chapter 3 and/or ability of the support to facilitate the movement of hydrogen across the surface following its dissociation on the Pd,²⁰ thus promoting the formation of Brønsted acid sites, which have been hypothesized as an active site for this reaction.⁴ A controlled deposition of Pd specifically onto the SiO₂-supported tungsten oxide species was attempted to increase the contact between Pd and WO_x species using a photo-deposition method (PD) and results from studies on that catalyst are discussed in **Appendix C**. While photodeposition of Pd marginally increased the formation rate of propanal and propanol relative to impregnation, its performance was still an order of magnitude lower than its P25-TiO₂-supported analogs.



Figure 4.5: Formation rate of propanal and propanol on a per mol W basis vs Pd weight percent over SiO₂ and P25-TiO₂ supported Pd-6W catalysts. (0.15 g of catalyst, catalysts pretreated in flowing N₂ at 673 K for 1 h, 423 K, 1 atm, 15 cm³min⁻¹ H₂, 1.6 kPa propionic acid, 2 h TOS)

Interestingly, when the SiO₂-supported catalysts were not pretreated prior to the reaction and/or purposefully hydrated, the rates did increase two to three-fold, as discussed in **Appendix C**; however, the rates of the hydrated catalysts were still lower than their P25-TiO₂ analogs. The clear difference in behavior between TiO₂ and SiO₂ as supports for Pd-W catalysts used in the reduction of propionic acid is significant and warrants further study.

4.4 Conclusions

The influence of support on the reduction of propionic acid to propanal and propanol was evaluated on Pd-promoted W catalysts supported on SiO₂ and TiO₂. High-resolution STEM imaging showed Pd particles in the nanometer size range on both supports. Separate components of the Pd and WO_x species were tested on both SiO₂ and P25-TiO₂ supports, as well as their physical mixtures. Without the presence of WO_x , P25-TiO₂- and SiO₂-supported Pd catalysts showed little activity, with Pd-P25-TiO₂ being 90 % selectivity to propanal and propanol, while its SiO₂ analog was only 24 % selective, at conversion levels of 0.9 % and 0.2 %, respectively. The P25-TiO₂ supported WO_x component showed 71 % selectivity to propanol at a very low rate while its SiO₂ counterpart was inactive. A physical mixture of Pd-SiO₂ and W-SiO₂ increased the propanal and propanol selectivity to 44 %, while the mixture of Pd-P25-TiO₂ and Pd-W-P25-TiO₂ increased the observed rate, greater than both of the separate components, while maintaining a >96 % selectivity to propanal and propanol. The co-impregnated catalysts were more active than their physical mixture analogs in general, with the Pd-W-SiO₂ catalyst showing 96 % selectivity to propanal and propanol, higher than all the SiO₂ supported systems, at 1 % conversion, while the Pd-W-P25-TiO₂ catalyst maintained a high level of selectivity to the aldehyde and aldehyde even with an increased level of conversion to 9.2 %. Kinetic measurements showed reaction orders of 0.3 and

zero in H₂ and propionic acid, respectively over the Pd-W-P25-TiO₂ catalyst. The nature of the silica surface prevented an accurate determination of kinetics on the SiO₂ supported catalyst. Furthermore, across a range of Pd loadings, the W-normalized rate of propanal and propanol formation was an order of magnitude higher on the P25-TiO₂-supported Pd-W catalysts compared to their SiO₂ analogs, highlighting the strong interaction between the WO_x species and the P25-TiO₂ support and the vital role of support in the reduction of propionic acid.

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Chapter 5: Conclusions and Future Work

5.1 Summary of Findings

Supported metal oxide catalysts for the conversion of oxygenates were investigated utilizing two probe reactions, ethanol to butadiene (ETB) and propionic acid reduction to propanal and propanol. First, Lewis acidic metal oxides including Ta, Y, Pr, and La oxide supported on SiO₂ or dealuminated Beta zeolite were examined as effective catalysts for the conversion of ethanol to butadiene when physically mixed with SiO₂-supported Ag nanoparticles. The cation identity was important to the product distribution of the ETB reaction. The Lewis acid strength of the cations was investigated via the decomposition of 2-propanol and was shown to follow general acid-base periodic trends based on cation size, charge, and oxide surface structure, where the oxide surface exposing Ta^{5+} is a stronger Lewis acid than that exposing La^{3+} , for example. This correlation showed the stronger Lewis acid cation, Ta, exhibited a product distribution favoring butadiene, while the least acidic cation, La, favored butanol and higher carbon chain C4+ products. Regardless of the difference in product selectivities over the various cations, the rate of formation of the coupling products per mol of cation, i.e., the site-time-yield (STY), remained relatively similar across the four cations. The same series of cations were then supported on dealuminated Beta zeolite (HBZ). Diffuse reflectance (DR) UV-Vis spectroscopy revealed a quantum size effect of supported Ta and Pr catalysts, which indicated the metal oxide species to have a higher degree of isolation (perhaps atomic isolation) when supported on the zeolite compared to SiO₂, while high angle annular dark-field (HAADF)-STEM confirmed the existence of 1-2 nm sized oxide domains for all four SiO₂-supported oxides. Additionally, X-ray photoelectron spectroscopy (XPS) showed

the support did not affect the electronic nature of the Lewis acid cations, with both SiO₂- and HBZsupported cations remaining in the same oxidation states. Most interestingly, the zeolite supported Lewis acid cations showed on average an order of magnitude higher STY to coupling products than their SiO₂ analogs, regardless of the cation identity, which warrants further investigation.

In the study of reducible metal oxides, supported tungsten oxide catalysts were investigated for the hydrodeoxygenation (reduction) of carboxylic acids to their corresponding aldehydes and alcohols. Characterization of supported (Pd)-WOx catalysts showed the nature of WOx species changes depending on support and thermal treatment. Acid-treatment of the SiO₂ support allows the formation of highly isolated WO_x species. The WO_x clusters on untreated SiO_2 are less dispersed and exist as primarily nanometer-sized WO_x clusters evident from DR UV-Vis spectroscopy and HAADF-STEM imaging. Titania-supported WO_x species are also highly dispersed on both P25 and rutile, with sub nanometer size clusters on P25 confirmed by HAADF-STEM imaging. In general, highly dispersed WO_x species can be synthesized on the two supports. The effect of support and cluster size on the reducibility of the tungsten oxide species was probed with H₂-TPR. Results showed that the addition of Pd on SiO₂-supported WO_x species aids the reduction of WO_x by decreasing the initial reduction temperature from 915 K to 600 K, while the initial reduction temperature remained the same on the P25-TiO₂ supported analog at around 600 K. In situ XPS and X-ray absorption spectroscopy probed the resulting oxidation states following various reducing treatments. The faciliated reduction of tungsten oxide through the addition of Pd on SiO₂-supported WO_x catalysts was confirmed by those methods, with W in WO_x species reducing from +6 to a mixture of +6 and +5 at lower temperatures, i.e., 600 K. Further reduction of W up to 1000 K showed a primarily +5 oxidation state, regardless of the Pd promotion. However, the fraction of +5 in the WO_x species supported on P25-TiO₂ that was identified by XPS remained unaffected at equal reducing treatments, even with the promotion of Pd. In situ XAS and quantum chemical calculations provided evidence that W in the WO_x species remain primarily in a +6 oxidation state. Thus, both X-ray techniques showed that the W in WO_x species does not appreciably change oxidation state under reducing conditions (5% H₂), in agreement with XPS. Computational results also provided evidence for the formation of Brønsted acid sites for larger WO_x clusters on SiO₂ and all of the cluster sizes tested (monomer, dimer, and trimer) on the TiO₂ supports (anatase and rutile) in the presence of H₂. Additionally, calculations showed that the tungsten oxide clusters prefer to remain in a tetrahedral configuration, regardless of the the support.

The influence of the two supports (SiO₂ vs TiO₂) on the reactivity of Pd promoted WO_x catalysts was then investigated for the reduction of propionic acid to propanal and propanol as a model system. Without the WO_x species present, P25-TiO₂- and SiO₂-supported Pd did show low background activity towards propanal and propanol formation, however it was negligible compared to their WO_x-loaded analogs, highlighting the importance of the active WO_x species. Interestingly, physical mixtures of the Pd and WO_x components on the same support, i.e., SiO₂supported Pd and SiO₂-supported WO_x, increased the conversion and selectivity to propanal and propanol, compared to the separate components, however, the co-impregnation of the Pd and WO_x on the same support produced a more active catalyst based on a relative formation rate of propanal and propanol. The comparison between SiO₂- and P25-TiO₂-supported Pd-W catalysts showed that while both had >95% selectivity towards propanal and propanol, the formation rate of those products, normalized by mol of W, was an order of magnitude higher on the P25-TiO₂ support, even across a wide range of Pd loadings, 0.2 wt% to 1 wt%. High resolution STEM imaging showed evidence of 2-5 nm Pd nanoparticles on the SiO₂-supported catalyst and a 5-10 nm Pd nanoparticle on the P25-TiO₂ support, suggesting that the dispersion of Pd did not affect the

activity. Instead, this higher activity may be due to strong interaction between the WO_x species and the P25-TiO₂ support. On the contrary, the rutile-TiO₂ supported Pd-W catalyst showed a fivefold lower rate compared to its P25-TiO₂ analog, again highlighting the influence of support in the reduction of propionic acid to propanal and propanol. Reaction kinetics of the P25-TiO₂-supported Pd-W catalyst showed reaction orders of 0.3 and zero in H₂ and propionic acid, respectively, with an apparent activation energy of 64 kJ mol⁻¹, which was in agreement with previously reported values. While the nature of SiO₂ support is interesting, an analogous non-reducible support may provide better results and insight into the influence of a reducible vs non-reducible support for this reaction and thus warrents further study.

5.2 Future Work

5.2.1 Lewis Acid Metal Oxides for the Conversion of Ethanol to C4+ Products. The conversion of ethanol to higher value products has been an ongoing research topic for the past few decades. With growing environmental concerns regarding emissions and CO₂ levels, there has been a push to utilize ethanol as the feedstock for the production of sustainable aviation fuel (SAF) through various reaction networks.^{1, 2} One possibility is butene oligomerization to form longer chain hydrocarbons which are in the hydrocarbon range for jet fuel, C9 to C16.³ The work presented here indicates that zeolite-supported metal oxides are beneficial in the conversion of ethanol to higher value products, such as 1,3-butadiene, butanol, or heavier C₄₊ compounds. In fact, groups have utilized similar Lewis acid catalysts, specifically Y and La, albeit with a few modifications such as the incorporation of Cu and Zn, to effectively convert ethanol to butene-rich products in the presence of H₂.^{4, 5} Some reports have even attempted to produce long chain hydrocarbons, C6 to C14 range, from a single catalyst with ethanol as the feedstock.² Instead of incorporating additional components such as Cu and Zn in the zeolite supported metal oxide, the same strategy

of separating the components as discussed in Chapter 2 can be applied to this process with Betazeolite-supported La, Y, or Pr as these cations being more selective to further coupling products, unlike Ta. Co-feeding H₂ with ethanol may increase the selectivity towards heavier coupling products, especially for the C4+ products.⁴ Thus it would be beneficial to understand if the metal oxide component, supported on the Beta zeolite, is selective to specifically butenes and even higher chain coupling products, in the presence of H₂ without the incorporation of Ag, Cu, or Zn on the same catalyst. These longer chain products or butenes can then be further utilized in the production of sustainable aviation fuel through oligomerization over a separate catalyst.⁶

5.2.1 Varying the Metal Oxide and Support for Spillover and Reduction of Carboxylic Acids to Aldehydes and Alcohols. Reducible metal oxides, such as WO_x are active catalysts for the conversion of carboxylic acids when promoted with a PGM, as is shown in Chapter 4. Even so, both ReO_x and MoO_x catalysts have also been shown to be active for such reactions.^{7, 8} As the support is shown to have an influence on both the reducibility and reactivity of the active tungsten oxide species, the choice of the active metal oxide may also affect the reactivity under identical conditions. Thus, investigating the activity of other oxides such as those of Ta and Pr may be beneficial in the context of this reaction. The use of an oxide such as TaO_x, which is generally regarded as non-reducible⁹ while still possessing the possibility of forming Brønsted acid sites in conjunction with Lewis acid sites,¹⁰ and PrO_x , which is a redox active oxide with +4 and +3 oxidation states,¹¹ may provide a more active catalyst for hydrodeoxygenation reactions when promoted with a PGM. Additionally, they could help elucidate which characteristic of the oxide is more important, i.e., reducibility or ability to form Brønsted acid sites potentially via hydrogen spillover from the PGM. Work from Chapter 3 and previous reports^{12, 13} have suggested that atomic hydrogen from the PGM may help form Brønsted acid sites on the WO_x species, which are

hypothesized as an active site in the reduction of propionic acid.¹⁴ Due to this, there is the likelihood that a similar formation of Brønsted acid sites may occur on other oxides, such as those of Ta and Pr. While a possibility of further reduction of an oxide species remains, as in the case of praseodymium oxide where Pr reduces from a +4 to +3 oxidation state, the reducibility can be investigated with H₂-TPR. Furthermore, investigation of the acid sites of these oxides can help determine whether the presence, quantity, or even strength of the Brønsted acid sites play a role in this reaction. Techniques such as DR-Fourier infrared spectroscopy utilizing pyridine as a titrating probe molecule or NH₃-temperature programmed desorption have been shown to be effective for acid site quantification.¹⁵⁻¹⁷ Likewise, due to the limitation of the silica support during transient kinetic experiments with Pd-W catalysts in Chapter 4, the use of Al₂O₃ as a non-reducible support may be beneficial in providing a clearer picture on the influence of support on the kinetics such as reaction orders and activation energies while also providing insight on the effect of spillover on such a support. However, the acidic nature of Al₂O₃¹⁷ should be taken into account as it may show background activity in the reaction, similar to that of the P25-TiO₂ support.

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Appendix A: Supporting Information for Chapter 2

A.1: Results and Discussion

and metal oxid	e catalysis by melpier	it wettiess impregnatio	11.				
			Therm	Thermal Treatment			
Catalyst	Precursor	Supplier & Purity	Temperatur e (K)	Time (h)	Ramp rate (K min ⁻¹)		
Ag-SiO ₂	AgNO ₃	Sigma-Aldrich, 99.0%	873	4	2		
Y-SiO ₂ or - HBZ	$Y(NO_3)_3 \cdot 6H_2O$	Aldrich, 99.9%	823	6	2		
Ta-SiO ₂ or - HBZ	(CH ₃ H ₂ O) ₅ Ta	Aldrich, 99.98%	773	5	5		
La-SiO ₂ or - HBZ	$La(NO_3)_3 \cdot 6H_2O$	Aldrich, 99.99%	823	6	2		
Pr-SiO ₂ or - HBZ	$Pr(NO_3)_3 \cdot 6H_2O$	Aldrich, 99.9%	823	6	2		
Na-HBZ	NaNO ₃	Fisher Scientific, 99.6%	773	6	2		
SiO ₂ -550	-	Sigma-Aldrich	823	6	2		
DeAl-HBZ- 550	-	ACS Material	823	6	2		

Table A1: Precursor used and thermal treatment parameters for synthesis of SiO₂-supported Ag and metal oxide catalysts by incipient wetness impregnation.

Thermal treatment parameters were based on the synthesis methods previously outlined by Dochain et al. for supported Ta catalysts^[1] and Qi et al. for supported Y catalysts^[2]. As the precursors for supported La and Pr catalysts were nitrates, as was the case for Y, the same thermal treatment parameters were used for Y, La, and Pr.

	mpoblicion or i					
Samula		XRF Composition (wt%)				
Sample	Metal	Cation				
Ag-SiO ₂	0.4					
$20Y-SiO_2$		22.4				
0.5Y-HBZ		0.2				
1Y-HBZ		0.5				

Table A2: XRF composition of select catalysts



Figure A1: X-ray diffraction patterns of **a**) Ta catalysts, **b**) Y catalysts, and **c**) HBZ and DeAl-HBZ supports as well as 2Y-HBZ catalyst. Patterns are offset for clarity.



Figure A2: High resolution HAADF-STEM images of two different areas of **a**) and **b**) 2Y-SiO₂, **c**) and **d**) 4La-SiO₂, as well as **e**) and **f**) 4Pr-SiO₂.



Figure A3: Example Tauc plots showing calculated direct bandgaps of **a**) 2Ta-SiO₂ and **b**) Pr₂O₃ bulk oxide reference.



Figure A4: Unnormalized DR UV-Vis spectra of 2Ta-SiO_2 catalyst under ambient conditions (blue) and following a pretreatment in 100 cm³·min⁻¹ He at 773 K for one hour (red); spectrum was recorded at 773 K.

Table A3: Effect of thermal treatment on band position and direct band gap of $2Ta-SiO_2$

Sample	Band Max (nm)	Direct Band Gap (eV)
2Ta-SiO ₂	228	5.0
773 K-1h	224	5.0

2Ta-SiO₂: spectra recorded at ambient conditions. 773 K-1h: spectra recorded after a 1 h hold at 773 K in flowing He.



Figure A5: Unnormalized DR UV-Vis spectra of Y-SiO₂ catalysts, with Y_2O_3 and SiO₂-550 shown for reference.



Figure A6: Unnormalized DR UV-Vis spectra of 4La-SiO₂ catalyst, with La₂O₃ and SiO₂-550 shown for reference.



Figure A7: Photoemission spectra in the O 2s region for **a**) SiO₂-550 and **b**) DeA1-HBZ-550 charge referenced to Si 2p at 103.5 eV.^[3]

Table A4: XI	PS peak fitting p	parameters for	the O 2s fea	ture of SiO ₂ -550	and DeAl
HBZ-550 sup	ports				

Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
SI6	SiO ₂ -550	O2s	25.4	4.4	100	6.4
	DeA1-HBZ- 550	O2s	25.4	4.6	100	6.5

catarysis						
Figure #	Sample	Band	Positio n	FWH M	%Area	Chi Squared
		00	25.4	2.0	(= 00	Squarea
		O2s	25.4	3.9	65.00	
	2Ta-	Ta 4f 7/2	27.2	2.5	20.00	3.3
	S10 ₂	Ta 4f 5/2	29.0	2.6	15.00	
2.4a		O2s	25.4	3.5	72.02	
	2Ta-	Ta 4f 7/2	27.4	2.4	15.99	3.5
	пв2	Ta 4f 5/2	28.9	2.5	11.99	

Table A5: XPS peak fitting parameters for 2Ta-SiO₂ and 2Ta-HBZ catalysts

catarysis						
Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
	2Y-	Y 3p 3/2	301.7	4.4	66.67	0.0
2.4h	SiO_2	Y 3p 1/2	313.6	4.3	33.33	0.9
2.4b	2Y-	Y 3p 3/2	301.7	6.0	66.67	1.0
	HBZ	Y 3p 1/2	312.7	6.3	33.33	1.9

Table A6: XPS peak fitting parameters for 2Y-SiO₂ and 2Y-HBZ catalysts

Table A7: XPS peak fitting parameters for $4Pr-SiO_2$ and 4Pr-HBZ catalysts

Figure	Sampla	Dand	Positio EWHM %A		0/ A roo	Chi
#	Sample	Dallu	n		/0Alea	Squared
		5/2 Sat.	930.3	3.8	20.5	
	4D.,	Pr 3d 5/2	934.2	3.9	40.86	
	4Pr-	3/2 Sat.	950.4	3.4	7.84	2.1
	5102	Pr 3d 3/2	954.6	4.6	27.38	
2.4-		3/2 S.U	958.9	2.6	3.44	
2.4C		5/2 Sat.	930.1	3.9	21.05	
	4D	Pr 3d 5/2	934.1	3.9	41.66	
	4Pr-	3/2 Sat.	950.6	2.3	5.00	1.5
	ΠΒΖ	Pr 3d 3/2	954.6	4.1	27.91	
		3/2 S.U	958.5	2.8	4.38	

Figure #	Sample	Band	Positio n	FWHM	%Area	Chi Squared
		La 3d 5/2	835.5	2.6	32.91	
	4La-	5/2 Sat.	838.8	2.8	22.41	83
	SiO ₂	La 3d 3/2	852.1	2.6	22.05	0.5
2.44		3/2 Sat.	855.4	3.9	22.64	
2.40 -		La 3d 5/2	835.7	3.2	34.89	
	4La-	5/2 Sat.	839.0	2.8	20.72	17
	HBZ	La 3d 3/2	852.3	2.9	23.27	1.7
		3/2 Sat.	855.6	3.8	21.12	

 Table A8: XPS peak fitting parameters for 4La-SiO2 and 4La-HBZ catalysts

		Selectivity (%)					
Catalyst	Conversion (%)	Ethylene + DEE	Acetaldehyde	1,3-Butadiene	Butanol	Other	
Ag-SiO ₂ ^a	26	3	97	-	-	-	
DeAl- HBZ	21	42	52	2	-	4	
4Na- HBZ	27	3	95	-	-	2	
0.5Y- HBZ	28	18	41	38	1	2	
1Y-HBZ	20	12	34	46	2	7	
1Y-HBZ ^b (x2)	38	23	19	52	1	5	
2Y-HBZ	27	9	33	44	4	10	

Table A9: Conversion and product distribution from ethanol reaction over Ag-SiO₂ and select catalysts physically mixed with Ag-SiO₂

^a0.1g of Ag-SiO₂, total catalyst amount = 0.15 g, 0.1 g of Ag-SiO₂ and 0.05 g of M-HBZ (0.1 g of 1Y-HBZ)^b, TOS = 4 h, T = 573 K, 6 % EtOH/94 % N₂

Table A10: Conversion and product distribution from ethanol reaction over Ta catalysts physically mixed with Ag-SiO₂

		Selectivity (%)						
Catalyst	Conversion (%)	Ethylene + DEE	Acetaldehyde	1,3-Butadiene	Butanol	Other		
2Ta-HBZ	30	28	61	9	-	3		
2Ta-SiO ₂	15	8	75	12	-	5		
4Ta-SiO ₂	20	14	65	19	-	2		
10Ta-SiO ₂	21	24	50	24	-	2		

Total catalyst amount = 0.5 g for Ta-SiO₂ systems and 0.15 g for Ta-HBZ systems (0.1 g of Ag-SiO₂ and 0.4 g of Ta-SiO₂ or 0.05 g of Ta-HBZ). TOS = 4 h, 573 K, 6 % EtOH/94 % N₂.

		Selectivity (%)					
Catalyst	Conversion (%)	Ethylene + DEE	Acetaldehyde	1,3-Butadiene	Butanol	Other	
2Y-HBZ	27	9	33	44	4	10	
2Y-SiO ₂	21	6	37	38	11	8	
4Y-SiO ₂	21	8	35	39	11	7	
20Y-SiO ₂	22	13	20	39	17	11	

Table A11: Conversion and product distribution from ethanol reaction over Y catalysts physically mixed with Ag-SiO₂

Total catalyst amount = 0.5 g for Y-SiO₂ systems and 0.15 g for Y-HBZ systems (0.1 g of Ag-SiO₂ and 0.4 g of Y-SiO₂ or 0.05 g of Y-HBZ). TOS = 4 h, 573 K, 6 % EtOH/94 % N₂.

Table A12: Conversion and product distribution from ethanol reaction over La and Pr catalysts physically mixed with Ag-SiO₂

		Selectivity (%)				
Catalyst	Conversion (%)	Ethylene + DEE	Acetaldehyde	1,3-Butadiene	Butanol	Other
4La-HBZ	16	8	46	38	4	4
4La-SiO ₂	17	3	49	14	19	15
4Pr-HBZ	20	9	36	47	3	5
4Pr-SiO ₂	14	5	50	22	12	11

Total catalyst amount = 0.5 g for M-SiO₂ systems and 0.15 g for M-HBZ systems (0.1 g of Ag-SiO₂ and 0.4 g of M-SiO₂ or 0.05 g of M-HBZ). TOS = 4 h, 573 K, 6 % EtOH/94 % N₂.



Figure A8: Site time yield of major products normalized per M cation (Ta, Y, La, or Pr), **a**) 1,3butadiene, **b**) butanol, and **c**) ethylene and diethyl ether, as a function of time on stream for M-SiO₂ catalyst systems physically mixed with Ag-SiO₂. Corresponding conversions (~ 14-21%) and product selectivity are shown in **Tables A9-A11**. Total catalyst amount = 0.5 g, 0.1 g of Ag-SiO₂ and 0.4 g of M-SiO₂, 573 K, 6 % EtOH/94 % N₂.



Figure A9: Site time yield of 1,3-butadiene normalized per M cation (Ta or Y) for **a**) SiO₂-supported Ta catalysts at various loadings, **b**) SiO₂-supported Y catalysts at various loadings, and **c**) HBZ-supported Y catalysts at various loadings, as a function of time on stream for M-SiO₂ or M-HBZ catalyst systems physically mixed with Ag-SiO₂. Conversion was ~ 15-28%, depending on catalyst. Corresponding conversions and product selectivities are shown in **Tables A9 and A10**. Total catalyst amount = 0.5 g, 0.1 g of Ag-SiO₂ and 0.4 g of M-SiO₂, 573 K, 6 % EtOH/94 % N₂.



Figure A10: Site time yield of butanol normalized per M cation (Y, Pr, or La) for **a**) SiO₂ supported Y catalysts at various loadings, **b**) SiO₂ and HBZ supported Y catalyst at equal loading and **c**) SiO₂ and HBZ supported La and Pr catalysts at equal loadings, as a function of time on stream for M-SiO₂ or M-HBZ catalyst systems physically mixed with Ag-SiO₂. Conversion was ~ 14-28%, depending on catalyst. Corresponding conversions and product selectivities are shown in **Tables A10 and A11**. Total catalyst amount = 0.5 g, 0.1 g of Ag-SiO₂ and 0.4 g of M-SiO₂, 573 K, 6 % EtOH/94 % N₂.

Reaction of 2-propanol over DeAl-HBZ and La-HBZ

The decomposition of 2-propanol was tested over DeAl-HBZ support along with 4La-HBZ, with results shown in Table A13. It should be noted, the conditions used for the support effect were different from those used for the cation effect due to the high reactivity of the zeolite support for dehydration. The propene formation rate was normalized by amount of catalyst, rather than mols of cation, due to absence of La on the DeAl-HBZ catalyst.

I able A13: 2-propanol decomposition over DeAI-HBZ and 4La-HBZ catalysts							
		Selectivity (%)		STY (mol i)·(g _{cat}) ⁻¹ (s) ⁻¹			
Catalyst	Conversion (%)	Propene	Diisopropyl ether	Propene (x10 ⁻⁶)	Diisopropyl ether (x10 ⁻⁷)		
DeAl- HBZ	31	93	7	13	5.0		
4La- HBZ	7.8	83	17	2.8	2.9		

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Catalyst amount = 0.01 g, TOS = 11 h, 473 K, 22 % 2-propanol/78 % N_2

The parent DeAl-HBZ showed 31% conversion along with 93% selectivity to propene and 7% selectivity to diisopropyl ether. Addition of La to the DeAl-HBZ support showed a drop of conversion from 31% to 8% with a greater selectivity to diisopropyl ether at 17%. The parent DeAl-HBZ had a STY of propene an order of magnitude greater than 4La-HBZ. This may suggest that open hydroxyl groups, residual aluminum, or residual Brønsted acid sites on the DeAl-HBZ are responsible for the high dehydration rates of 2-propanol, which coincides well with the formation of ethanol dehydration side products, ethylene and diethyl ether, in the ethanol to butadiene reaction. The addition of La onto the DeAl-HBZ support created Lewis acid sites while significantly decreasing the residual acidity of the dealuminated zeolite, thus lowering the dehydration rate of the catalyst.

A.2: References

[1] Dochain, D. D.; Stýskalík, A.; Debecker, D. P. Ag- and Cu-Promoted Mesoporous Ta-SiO₂
 Catalysts Prepared by Non-Hydrolytic Sol-Gel for the Conversion of Ethanol to Butadiene.
 Catalysts 2019, 9 (11). DOI: 10.3390/catal9110920.

[2] Qi, L.; Zhang, Y.; Conrad, M. A.; Russell, C. K.; Miller, J.; Bell, A. T. Ethanol Conversion to Butadiene over Isolated Zinc and Yttrium Sites Grafted onto Dealuminated Beta Zeolite. *J Am Chem Soc* 2020, *142* (34), 14674-14687. DOI: 10.1021/jacs.0c06906 From NLM PubMed-not-MEDLINE.

[3] Crist, V. B. Handbooks of Monochromatic XPS Spectra: Volume 2: Commercially Commercially Pure Binary Oxides; XPS International LLC, 2019. 637-639.

Appendix B: Supporting Information for Chapter 3

B.1: Supplemental Information for Experiments



Figure B1: Example Tauc plots showing calculated direct bandgap of 2W-AT-SiO₂ sample.

Sample	Pd	W
1Pd-WO ₃	0.8	99.2
1Pd-2W-AT-SiO ₂	0.3	2.6
2W-AT-SiO ₂	-	2.0
3W-SiO ₂	-	3.2
1Pd-3W-SiO ₂	0.5	3.1
6W-SiO ₂	-	6.6
1Pd-6W-SiO ₂	0.7	6.6
$1Pd-TiO_2$	0.4	-
3W-TiO ₂	-	3.3
$1Pd-3W-TiO_2$	0.5	3.0
6W-TiO ₂	-	5.2
1Pd-6W-TiO ₂	0.6	5.8

Table B1: X-ray Fluorescence composition of select samples by weight % of Pd and W



Figure B2: Additional high resolution HAADF-STEM images of a) 3W-SiO₂ and b) 6W-SiO₂ at a resolution of 2 and 1 nm, respectively.

Catalysis		
Sample	Band Gap (eV)	LMCT Band (nm)
Na ₂ WO ₄	5.1	225
2W-AT-SiO ₂	4.8	221
3W-SiO ₂	4.1	261
6W-SiO ₂	4.0	270
$(NH_4)_6H_2W_{12}O_{40}$	3.4	318
WO ₃	2.8	378

Table B2: Direct Bandgaps and LMCT positions of reference W materials and SiO₂ supported W catalysts



Figure B3: DR UV-Vis spectrum of P25-TiO₂ support and 3W-P25-TiO₂ showing the high absorption of the P25-TiO₂ support relative to WO_x species.



Figure B4: Normalized DR UV-Vis spectra of reference W materials and 3W-SiO₂ sample.



Figure B5: Additional high resolution HAADF-STEM images of a) 3W-P25-TiO₂ and b) 6W-P25-TiO₂ at a resolution of 5 and 2 nm, respectively.

select W catalysts	
Sample	Mol H ₂ /mol W
WO ₂	1.9
WO ₃	2.8
1Pd-WO ₃	2.7
1Pd-2W-AT-SiO ₂	0.9
2W-AT-SiO ₂	0.5
3W-SiO ₂	0.9
$1Pd-3W-SiO_2$	1.0
6W-SiO ₂	0.8
1Pd-6W-SiO ₂	1.1
6W-P25-TiO ₂	1.0*
1Pd-6W-P25-TiO ₂	1.5*

 Table B3: Hydrogen consumption per mol W for

Mol W calculated from XRF measurements listed in **Table B1.** *Background reduction of P25-TiO₂

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support.



Figure B6: Temperature-programed reduction profiles with a ramp rate of 10 K·min⁻¹ to 1223 K and hold for 20 min under a flow of 5% H₂/Ar at 30 cm³min⁻¹ of **a**) 1Pd-P25-TiO₂, P25-TiO₂, and R-TiO₂ samples.



Figure B7: Temperature-programed reduction profiles with a ramp rate of 10 K·min⁻¹ to 1223 K and hold for 20 min under a flow of 5% H₂/Ar at 30 cm³min⁻¹ of 1Pd-3W-SiO₂ and 3W-SiO₂ samples.



Figure B8: Temperature-programed reduction profiles with a ramp rate of 10 K·min⁻¹ to 1223 K and hold for 20 min under a flow of 5% H_2/Ar at 30 cm³min⁻¹ of 1Pd-2W-AT-SiO₂ and 2W-AT-SiO₂ samples.



Figure B9: Temperature-programed reduction profiles with a ramp rate of 10 K·min⁻¹ to 1223 K and hold for 20 min under a flow of 5% H₂/Ar at 30 cm³min⁻¹ of reference bulk WO₂ and WO₃ as well as 1Pd-WO₃ samples.

Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
5a	6W-SiO ₂	$W^{6+} 4 f_{7/2}$	36.7	2.5	57.14	1.1
		$W^{6+}4f_{5/2}$	38.9	2.5	42.86	1.1
	1Pd-6W-SiO ₂	$W^{5+}4f_{7/2}$	35.4	2.2	25.62	1.0
		$W^{5+}4f_{5/2}$	37.6	2.2	31.52	
		$W^{6+}4f_{7/2}$	36.6	2.2	19.22	1.8
		$W^{6+}4f_{5/2}$	38.7	2.2	23.64	

Table B4: XPS peak fitting parameters for 6W-SiO₂ and 1Pd-6W-SiO₂ samples following 600 K reducing treatment in 5% H₂/N₂.

Spacing between 7/2 and 5/2 peaks of each species was held constant at 2.18 eV.

FWHM value was set as equal across all peaks in each sample.

Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
5b -	6W-SiO ₂	$W^{5+}4f_{7/2}$	34.9	1.6	36.34	
		$W^{5+}4f_{5/2}$	37.0	1.6	20.80	1.6
		$W^{6+} 4 f_{7/2}$	36.5	1.6	27.26	
		$W^{6+}4f_{5/2}$	38.7	1.6	15.60	
	1Pd-6W-SiO ₂	$W^{5+}4f_{7/2}$	35.2	1.6	43.96	
		$W^{5+}4f_{5/2}$	37.4	1.6	13.18	2.6
		$W^{6+} 4 f_{7/2}$	36.6	1.6	32.97	5.0
		$W^{6+}4f_{5/2}$	38.8	1.6	9.88	

Table B5: XPS peak fitting parameters for 6W-SiO₂ and 1Pd-6W-SiO₂ samples following 800 K reducing treatment in 5% H₂/N₂.

Spacing between 7/2 and 5/2 peaks of each species was held constant at 2.18 eV.

FWHM value was set as equal across all peaks in each sample.

Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
5c -	6W-SiO ₂	$W^{5+}4f_{7/2}$	35.3	1.5	44.19	1.4
		$W^{5+}4f_{5/2}$	37.4	1.5	12.95	
		$W^{6+}4f_{7/2}$	36.7	1.5	33.14	1.4
		$W^{6+}4f_{5/2}$	38.9	1.5	9.71	
	1Pd-6W-SiO ₂	$W^{5+}4f_{7/2}$	35.1	1.4	45.77	
		$W^{5+}4f_{5/2}$	37.3	1.4	11.37	2.0
		$W^{6+}4f_{7/2}$	36.3	1.4	34.33	5.0
		$W^{6+}4f_{5/2}$	38.5	1.4	8.53	

Table B6: XPS peak fitting parameters for 6W-SiO₂ and 1Pd-6W-SiO₂ samples following 1000 K reducing treatment in 5% H₂/N₂.

Spacing between 7/2 and 5/2 peaks of each species was held constant at 2.18 eV. FWHM value was set as equal across all peaks in each sample.



Figure B10: In situ photoemission spectra and peak fits of the Pd 3d region for 1Pd-6W-SiO₂ sample **a**) prior to (fresh) and following a treatment in 5% H_2/N_2 at 30cm³min⁻¹ at **b**) 400 K and **c**) 600 K. Spectra were charge referenced to the Si 2p peak at 103.5 eV.
Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
	Freeh	$Pd^{2+} 3d_{5/2}$	336.8	2.0	59.88	0.85
	FICSH	$Pd^{2+} 3d_{3/2}$	342.0	2.3	40.12	0.85
SI10		$Pd^0 3d_{5/2}$	334.8	1.6	32.30	
	400 K	$Pd^0 3d_{3/2}$	340.1	1.6	21.64	1 10
		$Pd^{2+} 3d_{5/2}$	336.0	2.4	27.58	1.19
		$Pd^{2+} 3d_{3/2}$	341.3	2.5	18.48	
	600 V	$Pd^{0} 3d_{5/2}$	335.2	1.6	59.88	1.09
	600 K	$Pd^0 3d_{3/2}$	340.4	1.2	40.12	1.08

Table B7: XPS peak fitting parameters for the Pd 3d region on the 1Pd-6W-SiO₂ sample prior to (fresh) and following a 400 K and 600 K reducing treatment in 5% H_2/N_2 .

Spacing between 5/2 and 3/2 peaks of each species was held constant at 5.26 eV.



Figure B11: In situ photoemission spectra of normalized Ti 2p region for P25-TiO₂ support prior to and following a treatment in 5% H_2/N_2 at 30cm³min⁻¹ at 400, 600, 800, and 1000 K. Spectra were charge referenced to the Ti 2p peak at 458.7 eV.



Figure B12: In situ photoemission spectra of normalized Ti 3p region for P25-TiO₂ support prior to and following a treatment in 5% H_2/N_2 at 30cm³min⁻¹ at 400, 600, 800, and 1000 K. Spectra were charge referenced to the Ti 2p peak at 458.7 eV.



Figure B13: In situ photoemission spectra and peak fits of the W4f (and Ti 3p) region for 6W-P25-TiO₂ of the as-synthesized sample. Spectra were charge referenced to the Ti $2p_{3/2}$ peak at 458.7 eV.

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Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
		$W^{5+}4f_{7/2}$	35.4	1.2	32.16	
B13	6W-P25-	$W^{5+}4f_{5/2}$	37.6	1.2	24.12	5.2
	TiO_2 $Ti^{4+} 3p_{3/2}$	36.9	1.6	29.15	5.5	
		$Ti^{4+} 3p_{1/2}$	37.8	1.6	14.57	

Table B8: XPS peak fitting parameters for 6W-P25-TiO₂ sample as-synthesized and without a reducing treatment.

Spacing between W4f 7/2 and 5/2 peaks of each species was held constant at 2.18 eV. FWHM value was set as equal across all peaks in each sample. Ti 3p peaks were held constant based on fitting of bare P25-TiO₂ support in **Figure B12**.

Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
		$W^{5+}4f_{7/2}$	35.4	1.2	30.92	
	6W-P25-	$W^{5+}4f_{5/2}$	37.6	1.2	23.19	10.2
3.6a	TiO ₂	$Ti^{4+} 3p_{3/2}$	36.9	1.8	26.23	12.5
		$Ti^{4+} 3p_{1/2}$	37.9	1.8	19.67	
		$W^{5+}4f_{7/2}$	35.3	1.4	33.85	
	1Pd-6W-P25-	$W^{5+}4f_{5/2}$	37.5	1.4	25.39	26.9
	TiO ₂	TiO ₂ Ti ⁴⁺ $3p_{3/2}$ 36.9	1.6	27.18	20.8	
		$Ti^{4+} 3p_{1/2}$	37.9	1.6	13.59	

Table B9: XPS peak fitting parameters for $6W-P25-TiO_2$ and $1Pd-6W-P25-TiO_2$ samples following 600 K reducing treatment in 5% H₂/N₂.

Spacing between W4f 7/2 and 5/2 peaks of each species was held constant at 2.18 eV.

FWHM value was set as equal across all peaks in each sample. Ti 3p peaks were held constant based on fitting of bare P25-TiO₂ support in **Figure B12**.

Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
3.6b		$W^{5+}4f_{7/2}$	35.4	1.2	31.56	
	6W-P25-	$W^{5+}4f_{5/2}$	37.6	1.2	23.67	67
	TiO ₂	$Ti^{4+} 3p_{3/2}$	36.8	1.8	29.85	0.7
		$Ti^{4+} 3p_{1/2}$	37.8	1.8	14.93	
	-	$W^{5+}4f_{7/2}$	35.4	1.2	31.29	
	1Pd-6W-P25-	$W^{5+}4f_{5/2}$	37.6	1.2	23.46	174
	TiO ₂	$Ti^{4+} 3p_{3/2}$	36.8	1.6	30.17	1/.4
		$Ti^{4+} 3p_{1/2}$	37.8	1.6	15.1	

Table B10: XPS peak fitting parameters for $6W-P25-TiO_2$ and $1Pd-6W-P25-TiO_2$ samples following 800 K reducing treatment in 5% H₂/N₂.

Spacing between W4f 7/2 and 5/2 peaks of each species was held constant at 2.18 eV. FWHM value was set as equal across all peaks in each sample. Ti 3p peaks were held constant based on fitting of bare P25-TiO₂ support in **Figure B12**.

Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
		$W^{5+}4f_{7/2}$	35.4	1.3	33.55	
	6W-P25-	$W^{5+}4f_{5/2}$	37.6	1.3	25.17	5.2
2.6	TiO ₂	$Ti^{4+} 3p_{3/2}$	36.8	1.5	27.52	5.5
		$Ti^{4+} \; 3p_{1/2}$	37.8	1.6	13.76	
5.00		$W^{5+}4f_{7/2}$	35.5	1.1	30.09	
	1Pd-6W-P25-	$W^{5+}4f_{5/2}$	37.7	1.1	22.57	4.0
	TiO ₂	$Ti^{4+} 3p_{3/2}$	36.8	1.8	31.56	4.8
		$Ti^{4+} 3p_{1/2}$	37.8	1.7	15.78	

Table B11: XPS peak fitting parameters for $6W-P25-TiO_2$ and $1Pd-6W-P25-TiO_2$ samples following 1000 K reducing treatment in 5% H₂/N₂.

Spacing between W4f 7/2 and 5/2 peaks of each species was held constant at 2.18 eV. FWHM value was set as equal across all peaks in each sample. Ti 3p peaks were held constant based on fitting of bare P25-TiO₂ support in **Figure B12**.



Figure B14: In situ photoemission spectra and peak fits of the Pd 3d region for 1Pd-6W-P25-TiO₂ sample **a**) prior to (fresh) and following a treatment in 5% H_2/N_2 at 30cm³min⁻¹ at **b**) 400 K and **c**) 600 K. Spectra were charge referenced to the Ti 2p peak at 458.7 eV.

Figure #	Sample	Band	Position	FWHM	%Area	Chi Squared
B14	Fresh	$Pd^{2+} 3d_{5/2}$	336.3	1.7	59.88	1 58
	Presir	$Pd^{2+} 3d_{3/2}$	341.6	1.9	40.12	1.56
		$Pd^0 3d_{5/2}$	334.7	1.4	33.81	
	400 K	$Pd^0 3d_{3/2}$	340.0	1.4	22.65	1 1 4
		$Pd^{2+} 3d_{5/2}$	335.8	2.9	26.07	1.14
		$Pd^{2+} 3d_{3/2}$	341.1	3.1	17.47	
	600 V	$Pd^0 3d_{5/2}$	335.0	1.2	59.88	1 11
	000 K	$Pd^0 3d_{3/2}$	340.3	1.2	40.12	1.11

Table B12: XPS peak fitting parameters for the Pd 3d region on the 1Pd-6W-P25-TiO₂ sample prior to (fresh) and following a 400 K and 600 K reducing treatment in 5% H₂/N₂.

Spacing between 5/2 and 3/2 peaks of each species was held constant at 5.26 eV.

Table B13: Phase Composition by Weight % of TiO_2 Samples Calculated from Rietveld Refinementvia X-ray diffraction patterns from Figure B15

Sample	Anatase	Rutile
TiO ₂ -P25-NP	91	9
TiO ₂ -P25	76	24
6W-TiO ₂	89	11



Figure B15: X-ray diffraction patterns of 6W-P25-TiO₂, P25-TiO₂-(NP), and R-TiO₂. Intensity offset for clarity. P25-TiO₂ was calcined at 923 K in 100 cm³min⁻¹ flowing medical air (Praxair) for 4 h. P25-TiO₂-NP coincides with TiO₂ support that had no pretreatment prior to characterization. R-TiO₂ also had no pretreatment prior to characterization.

Sample	Normalized E (eV)	Oxidation State
W Metal	10207.0	0
WO_2	10208.1	4
WO ₃	10209.0	6
1Pd-6W-SiO ₂		
Before TPR	10208.8	5.7
At 773 K	10208.2	4.3
After TPR	10208.2	4.3
6W-SiO ₂		
Before TPR	10209.1	6.2
At 773 K	10208.9	5.8
After TPR	10208.8	5.7
1Pd-6W-TiO ₂		
Before TPR	10208.7	5.5
At 773 K	10208.5	5.0
After TPR	10208.6	5.3
6W-TiO ₂		
Before TPR	10208.8	5.7
At 773 K	10208.6	5.3
After TPR	10208.6	5.3

Table B14: Position of the W L_{III} edge at $\mu(E) = 1$ for various samples and standards. The corresponding oxidation states are reported as well after using the calibration curve in **Figure B16**.



Figure B16: Position of the L_{III} edge of W for each standard sample (W Foil, WO₂, and WO₃) at $\mu(E) = 1$. The corresponding oxidation state for each sample is plotted on the y-axis. The calibration curve was used to interpolate the oxidation state of the prepared samples presented in **Table B14**.



Figure B17: Ambient ex situ XANES spectra of the standard W samples at the W L_{III} edge.



Figure B18: In-situ XANES spectra of the W L_{III} edge before and after a TPR at 773 K under a flow of 5% H₂/N₂ at 20 cm³min⁻¹ of 6W-SiO₂.



Figure B19: In-situ XANES spectra of the W L_{III} edge before and after a TPR at 773 K under a flow of 5% H_2/N_2 at 20 cm³min⁻¹ of 6W-P25-TiO₂.

B.2: Generation of tungsten oxide clusters on silica

To represent different-sized tungsten oxide clusters, we used W monomers, dimers, and trimers. Grafting these clusters onto the SiO₂ surface requires the removal of at least one surface H atom, enabling W to bind with the surface O atoms. Various grafting configurations were explored by removing between 1 and 4 H atoms from the top of the SiO₂ slab and attaching W to the surface O atom(s). We generated initial W clusters where all W atoms exhibit formal oxidation states of +5 or +6, a choice made based on reported oxidation states for supported W-oxides following high temperature oxidative pretreatments. After grafting a W atom to surface O atom(s), additional O atom(s) and (or) OH group(s) were attached to W to achieve a formal oxidation state of +5 or +6. A maximum limit of 2 -OH groups is set because additional -OH groups would most likely lead to dehydration because of strong thermodynamic drive to form H₂O. Below, we show all generated configurations for monomers, dimers, and trimers, along with the oxidation state of all W in the cluster and the calculation of the relative free energy. White background species indicate the starting species in **Figure 3.9** in the main text.

Monomers:



Figure B20: Different configurations of WO_3 monomer supported on silica with +5 and +6 oxidation states. Number on left indicates the number of H atoms on the surface.



Figure B21: Energy hull diagram for the different configurations considered in **Figure B20** under synthesis conditions (0.01 kPa H₂O and 20 kPa O₂). 6H-1a and 6H-1b indicate different 3D configurations of the same stoichiometry. 1, 2, 3 indicate the first, second and third configuration in **Figure B20**. 4,5,6,7 indicate the number of H atoms on the surface.

Dimers:



Figure B22: Different configurations of WO_3 dimer supported on silica with +5 and +6 oxidation states. Number on left indicates the number of H atoms on the surface.



Figure B23: Energy hull diagram for the different configurations considered in **Figure B22** under synthesis conditions (0.01 kPa H₂O and 20 kPa O₂). 6H-1a and 6H-1b indicate different 3D configurations of the same stoichiometry. 1, 2, 3 indicate the first, second and third configuration in **Figure B22**. 4,5,6,7 indicate the number of H atoms on the surface.

Trimers



Figure B24: Different configurations of WO₃ trimer supported on silica with +5 and +6 oxidation states. Number on left indicates the number of H atoms on the surface.



Figure B25: Energy hull diagram for the different configurations considered in **Figure B24** under synthesis conditions (0.01 kPa H₂O and 20 kPa O₂). 6H-1a and 6H-1b indicate different 3D configurations of the same stoichiometry. 1, 2, 3 indicate the first, second and third configuration in **Figure B24**. 4,5,6,7 indicate the number of H atoms on the surface.

B.3: Phase diagrams and oxidation state using SCAN



Figure B26: Ab initio thermodynamic phase diagram for silica supported WO₃ monomer, dimer, and trimer at $P_{H2O} = 0.01$ kPa. Gray boxes report the oxidation state of W.



Figure B27: a) Ab initio thermodynamic phase diagram for rutile TiO₂ supported WO₃ monomer, dimer, and trimer. **b)** Ab initio thermodynamic phase diagram for anatase TiO₂ supported WO₃ monomer, dimer, and trimer. Gray boxes report the oxidation state of W.

S.3.1: Vacancy generation on rutile TiO₂



Rutile – TiO₂ support

Figure B28: Ab initio thermodynamic phase diagram for rutile TiO₂ supported WO₃ monomer, and dimer with surface O vacancies.

To generate O vacancies on the surface, we started from the structure with no initial surface vacancy that appeared on the phase diagram. We then systematically removed surface O atoms that were within 2.3 Å of the W atom, based on reported bond lengths for W clusters. Each of these structures is optimized using the same conversion criteria as previously reported in **Section 3.2.3**. We then take the structure with the lowest energy for each speciation and generate the phase diagram following the methods described in **Section 3.2.3**. Our results indicate that the presence of surface vacancies does not change the trend in the speciation of the W monomer and dimer clusters supported on rutile TiO_2 .



Figure B29: Ab initio thermodynamic phase diagram for monomer supported on β -crystabolite-SiO₂ (001) compared to amorphous silica supported monomer.

B.3.2: Phase diagrams for combined domain sizes



Figure B30: Energy hull diagram for all sizes of tungsten oxide cluster on silica support under a) synthesis conditions and b) reaction conditions. These figures contain all structures initially generated and from cascade reactions for H addition and O removal shown in **Figure 3.9**.



Figure B31: Energy hull diagram for all sizes of tungsten oxide cluster on both anatase and rutile titania support under a) synthesis conditions and b) reaction conditions. These figures contain all structures initially generated and from cascade reactions for H addition and O removal shown in **Figure 3.11**.

B.4: Density of States

B.4.1: WO₃ supported on silica with SCAN



Figure B32: Integrated Density of States for WO₃ monomer speciation supported on silica generated using SCAN. Compared to the HSE analysis shown in **Figure B33b**, the integrated DOS to Fermi Level (shifted to 0) does not show a significant difference.

B.4.2: WO₃ supported on silica



Figure B33: Density of States for WO₃ monomer speciation supported on silica. a) Projected density of states for W atoms. b) Integrated density of states for W atoms.



Figure B34: Density of States for WO₃ dimer speciation supported on silica. a) Projected density of states for W atoms. b) Integrated density of states for W atoms.



Figure B35: Density of States for WO₃ trimer speciation supported on silica. a) Projected density of states for W atoms. b) Integrated density of states for W atoms.

B.4.3: WO₃ supported on rutile titania



Figure B36: Density of States for WO₃ monomer speciation supported on rutile titania. a) Projected density of states for W atoms. b) Integrated density of states for W atoms.



Figure B37: Density of States for WO₃ dimer speciation supported on rutile titania. a) Projected density of states for W atoms. b) Integrated density of states for W atoms.



Figure B38: Density of States for WO₃ trimer speciation supported on rutile titania. a) Projected density of states for W atoms. b) Integrated density of states for W atoms.

B.4.4: WO3 supported on anatase titania



Figure B39: Density of States for WO₃ monomer speciation supported on anatase titania. a) Projected density of states for W atoms. b) Integrated density of states for W atoms.



Figure B40: Density of States for WO_3 dimer speciation supported on anatase titania. a) Projected density of states for W atoms. b) Integrated density of states for W atoms.



Figure B41: Density of States for WO₃ trimer speciation supported on anatase titania. a) Projected density of states for W atoms. b) Integrated density of states for W atoms.



B.5: Charge differences for O removal reaction

Figure B42: Differences in charge density of surface atoms on anatase and rutile titania support.



Figure B43: Differences in charge density of surface atoms on silica support. There are no silica atoms with charge differences, hence the lack of yellow bars in the figure.

Appendix C: Supporting Information for Chapter 4

C.1: Methods

Dinitrogen Physisorption. Surface areas were obtained by physisorption of N₂ (Praxair, 99.999%) at 77 K with a Micromeritics ASAP 2020 Plus instrument utilizing the BET method. Sample sizes of 150-300 mg were used for analysis. Prior to analysis, each sample was evacuated at 723 K under vacuum.

Catalyst Synthesis. A silica-supported catalyst was also prepared by a photo deposition (PD) method. In this method, we attempted to photoexcite the silica-supported tungsten oxide clusters (having a UV-Vis absorption band at ~270 nm, **Figure 3.2**) in an effort to photoreduce the aqueous Pd precursor on or near the tungsten clusters. A solution of 13M nitric acid (VWR, 69-70%) was added to DI H₂O until the solution reached a pH of 4 to reduce the likelihood of electrostatic deposition of the Pd onto the silica.^[1] The desired amount of the already synthesized 6W-SiO₂ sample was mixed into the acid solution for 30 min after which the Pd precursor was added. A UV filter for 280 nm (Newport, GSQ-WG280) was placed in front of the solution and a xenon arc lamp (ILC Technologies) was used as the light source. The light passed through an aqueous copper sulfate solution and the UV cutoff filter prior to entering the photodeposition reactor. The solution was irradiated for 4 h, after which the catalyst was washed with DI H₂O to a pH of 6, filtered and dried in air. The same drying and thermal treatment conditions were used as for the previously mentioned SiO₂ supported catalysts.

Hydrated SiO₂ samples (xPd-6W-SiO₂-H) utilized already synthesized Pd-6W-SiO₂ catalysts from IWI. The catalyst was exposed to 100% relative humidity at ambient temperature and pressure for 48 h.

C.2: Results and Discussion

Table C1: BET surface areas of TiO ₂ supports obtained from N ₂ -physisorption						
Sample	BET Surface Area (m ² ·g ⁻¹)					
P25-TiO ₂	58					
Rutile-TiO ₂	35					

Table C2: Elemental analysis and H₂ chemisorption values of 0.2Pd-6W-SiO₂-PD catalyst

	XRF Con	mposition	H ₂ -Chemisorption
Sample	(w	t%)	
_	Pd	W	% Metal Exposed
0.2Pd-6W-SiO ₂ -PD	0.2	4.7	34.8



Figure C1: High resolution HAADF-STEM images and elemental mapping for Pd and W over the same region of 0.2Pd-6W-SiO₂-PD catalyst following an N₂ pretreatment at 673 K for 1 h. Sample was exposed to ambient air for a limited time during transportation.

Table C3: Conversion	and product	distribution	from propi	onic acid r	eduction of	over the 0.2	2Pd-
6W-SiO ₂ -PD catalyst							

Cotolyst	Conversion	Selectivity					
Catalyst	Conversion -	LHC	DPE	Propanal	Propanol		
0.2Pd-6W-P.D	0.8	1	0	9	90		
0.15 g of catalyst, catalysts pretreated in flowing N ₂ at 673 K for 1 h, 423 K, 1 atm, 15							
cm ³ min ⁻¹ H ₂ , 1.6 kPa propionic acid, 2 h TOS							


Figure C2: Formation rate of propanal and propanol on a per mol W basis over SiO₂, R-TiO₂, P25-TiO₂-supported 0.2Pd-6W catalysts. (0.15 g of catalyst, catalysts pretreated in flowing N₂ at 673 K for 1 h, 423 K, 1 atm, 15 cm³min⁻¹ H₂, 1.6 kPa propionic acid, 2 h TOS)

Comparison of the formation rate of propanal and propanol across different supports is shown in **Figure C2**. We tried to direct the location of Pd with the photo-deposited catalyst (PD). Both H_2 chemisorption and microscopy (**Figure C1**) show there are still nm sized particles of Pd, which are typically larger than the tungsten oxide clusters. However, the slightly higher rate of the PD catalyst relative to its impregnated analog did warrant further studies as this type of synthesis on a support is seldom reported in literature. Instead of testing the catalysts with an inert pretreatment, the catalysts were tested as is without any pretreatment (**Figure C3**) and we found that the rate on the impregnated SiO₂ supported catalyst had slightly increased. The impregnated catalyst was then hydrated, which further increased the rate, now an order of magnitude higher compared to one with a N₂ pretreatment at 673 K. Likewise, the rate of propanal and propanol formation was also an order of magnitude higher for the PD catalyst without the pretreatment relative to one with and even showing the same rate as its P25-TiO₂ analog. We do note that the pretreatment conditions had no effect on the P25-TiO₂ supported catalysts (**Figure C4**). This rate increase on the SiO₂

supported catalysts is likely due to the effect of surface H₂O, which affects the surface concentration of a propoxy species bound to the surface of SiO₂, which then leads to the alcohol, propanol in this case. This is shown in previous work on a Pd-Re-SiO₂ catalyst during the same reaction. Upon an introduction of a water co-feed, there was an initial increase in the formation rate of propanol, followed by a decay to steady state values over the course of 5-10 hours.^[2] We do note both hydrated and pretreated SiO₂ supported catalysts take 2-3 hours to reach steady state and do not show deactivation over 14 hours on stream (Figures C5 and C6). This further indicates that transient kinetics on a clean (dehydrated) SiO₂ surface are limited in their use due to the nature of alcohols sticking on the surface, which is not the case with the TiO₂ support. The reaction orders on a pretreated Pd-W-SiO₂ catalyst were zero order in both propionic acid and H₂ (Figure C7). While the effect of acid pressure holds true to the P25-TiO₂ supported analog (Figure 4.4), the difference in the H₂ reaction order is likely due to the poor transient behavior of SiO₂ supported catalysts. This is further justified when the reaction orders were tested on a non-pretreated PD sample (Figure C8). In that case, the orders matched closely with that of the P25-TiO₂ support, suggesting surface H₂O likely plays a major role in preventing the alcohols from saturating the surface as previously mentioned.



Figure C3: Formation rate of propanal and propanol on a per mol W basis over SiO₂ supported 0.2Pd-6W catalysts. 1D represents 1 day in vial following synthesis, 1 M = 1 month, H = hydrated sample (see section C1) (0.15 g of catalyst, catalysts purged in flowing N₂ while reactor was heated to reaction temperature at 423 K, 1 atm, 15 cm³min⁻¹ H₂, 1.6 kPa propionic acid, 2 h TOS)



Figure C4: Effect of N₂ pretreatment on the formation rate of propanal and propanol on a per mol W basis over $0.2Pd-6W-P25-TiO_2$ catalysts. 0.15 g of catalyst, no pretreatment means catalyst was purged in flowing N₂ while reactor was heated to reaction temperature at 423 K, 1 atm, 15 cm³min⁻¹ H₂, 1.6 kPa propionic acid, 2 h TOS)



Figure C5: Product selectivity and conversion vs time on stream over $0.2Pd-6W-SiO_2$ catalyst. (catalysts pretreated in flowing N₂ at 673 K for 1 h, 423 K, 1 atm, 15 cm³min⁻¹ H₂, 1.6 kPa propionic acid)



Figure C6: Product selectivity and conversion vs time on stream over $0.2Pd-6W-SiO_2-H$ catalyst without pretreatment. (catalysts were purged in flowing N₂ while reactor was heated to reaction temperature, 423 K, 1 atm, 15 cm³min⁻¹ H₂, 1.6 kPa propionic acid)



Figure C7: Formation rate of propanol and propanal as a function of **a**) propionic acid pressure (0.15g of catalyst, 433 K, 1 atm, 15 cm³min⁻¹ H₂) **b**) H₂ pressure (0.45 g of catalyst, 433 K, 1 atm, 50 cm³min⁻¹ total flow of H₂ +N₂, 1.6 kPa propionic acid) and **c**) temperature (0.15g of catalyst, 1 atm, 15 cm³min⁻¹ H₂, 1.6 kPa propionic acid) over 0.5Pd-6W-SiO₂. (Catalysts were pretreated in flowing N₂ at 673 K for 1 h.) Numbers above data points represent order in which they were taken.



Figure C8: Formation rate of propanal and propanol as a function of **a**) propionic acid pressure (423 K, 1 atm, 60 cm³min⁻¹ H₂) **b**) H₂ pressure (423 K, 1 atm, 60 cm³min⁻¹ total flow of H₂ +N₂, 1.6 kPa propionic acid) and **c**) temperature (1 atm, 60 cm³min⁻¹ H₂, 1.6 kPa propionic acid) over 0.2Pd-6W-SiO₂-PD. (All reactions used 0.15 g of catalyst and catalysts were purged in flowing N₂ while reactor was heated to reaction temperature.)



Figure C9: Effect of catalyst amount on the formation rate of propanal and propanol on a per mol W basis over $0.5Pd-6W-SiO_2$ catalyst. (catalysts pretreated in flowing N₂ at 673 K for 1 h, 433 K, 1 atm, 50 cm³min⁻¹ H₂ for 0.45g and 60 cm³ min⁻¹ H₂ for 0.25g, 1.6 kPa propionic acid, 2 h TOS)

C.3: References

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