Relating the Structure of Bimetallic Catalysts to Performance in the Hydrogenolysis and Hydrogenation of Biomass-Derived Intermediates

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Derek D. Falcone

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Author – Derek D. Falcone

The dissertation has read and approved by the examining committee:

Advisor – Robert J. Davis

Chemical Engineering – Gary M. Koenig Jr.

Chemical Engineering – David L. Green

Chemical Engineering – Joshua J. Choi

Chemistry – Ian Harrison

Accepted for the School of Engineering and Applied Science:

Dean – James H. Aylor

Abstract

The addition of a second metal to supported metallic nanoparticles produces a range of unique catalytic properties by altering the structural and chemical properties of the catalytic surface. Elucidating the structure and function of supported bimetallic nanoparticles is therefore crucial to enable the rational design of new and improved catalysts for the production of fuels and chemicals from molecular-derivatives of renewable biomass.

In this work, the presence of copper on titania-supported Ru nanoparticles was observed to increase the selectivity of glycerol hydrogenolysis to 1,2-propanediol. Characterization of catalysts by H₂ chemisorption, X-ray diffraction, scanning transmission electron microscopy and X-ray photoelectron spectroscopy suggested that both Ru and Cu were present on the surface of the titania-supported bimetallic nanoparticles. By normalizing conversion rate to the number of surface Ru atoms, the presence of Cu was shown to decrease the rate of glycerol hydrogenolysis slightly while increasing selectivity to 1,2-propanediol from 48% on monometallic Ru to over 90% on Ru-Cu. Copper likely diluted large Ru ensembles that are responsible for C-C bond cleavage leading to ethylene glycol instead of the desired 1,2-propanediol. The presence of Cu also inhibited the deactivation exhibited by monometallic Ru presumably by limiting the formation of strongly adsorbed C_xH_y species produced on large Ru ensembles.

The addition of Re to supported Pt catalysts promoted the rate of glycerol hydrogenolysis to propanediols in liquid water by more than an order of magnitude and shifted the initial product selectivity from predominantly 1,2-propanediol to a mixture of

1,2 and 1,3-propanediols. A combination of conventional and near-ambient-pressure X-ray photoelectron spectroscopy revealed that a range of Re oxidation states, as well as metallic Pt, were present on the surface of the Pt-Re catalysts after reduction in H₂ at 393 and 493 K, even though reduction of Re was enhanced by the Pt.

Infrared spectroscopy of adsorbed pyridine and the aqueous-phase hydrolysis of propyl acetate were used to identify and characterize Brønsted acid sites present on the Pt-Re bimetallic catalyst after reduction in H_2 at 473 K. Normalizing the rate of propyl acetate hydrolysis over Pt-Re to the rate in aqueous HCl, enabled the quantification of approximately 6% of the Re atoms that formed catalytically-active Brønsted acid sites.

Given the observation of both reduced Pt sites and Brønsted acid sites on the bifunctional Pt-Re catalyst, a proposed mechanism of glycerol hydrogenolysis involving acid-catalyzed dehydration followed by Pt-catalyzed hydrogenation of the unsaturated intermediate was supported by the negative influence of added base, a primary kinetic isotope effect with deuterated glycerol, an inverse isotope effect with dideuterium gas, and the observed orders of reaction with respect to glycerol and dihydrogen.

The inverse kinetic isotope effect obtained with dideuterium gas indicated that hydrogenation was not a kinetically relevant step for glycerol hydrogenolysis over Pt-Re. To confirm the kinetic insignificance of C=C and C=O bond hydrogenation in the glycerol hydrogenolysis mechanism, the low temperature hydrogenation of methyl vinyl ketone, crotonaldehyde, 2-butanone, and butanal was performed over Pt-Re. The presence of Re on Pt decreased the rate of C=C bond hydrogenation but enhanced the rate of C=O bond hydrogenation. Because the rates of double bond hydrogenation were higher than the rate

of glycerol hydrogenolysis, hydrogenation is most likely a kinetically insignificant component of the hydrogenolysis reaction path.

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Chapter 1: Introduction and Motivation

1.1 Production of Chemicals from Renewable Biomass

Anthropogenic production of CO_2 is a formidable environmental concern. The high concentration of CO_2 in the atmosphere, which has increased dramatically since the start of the industrial revolution, has led scientists, policy makers, and advocates to explore using renewable biomass as a source of carbon to produce the fuels and chemicals on which our world relies. In 2014, 82% of the world's energy consumption consisted of fossil sources, which unleashed approximately 5.4 billion metric tons of CO_2 into the atmosphere¹. Utilizing biomass to produce fuels and chemicals, which normally require petroleum as a feedstock, may assist in decreasing atmospheric CO_2 because it is a more carbon neutral process^{2–4}. Carbon that is released from the combustion of fuel will be fixed more quantitatively into the carbon cycle by photosynthesis producing more biomass.

At the current petroleum prices (WTI was \$48/bbl as of July, 2015) it is significantly cheaper to use fossil sources to produce fuel in the United States than biomass. If the price of petroleum remains at or near the current levels then the production of biogasoline and bio-diesel will never be economically competitive in the United States unless regulations are enacted. In addition, the efficiency of automobiles is continuing to improve and people in the United States are driving fewer miles. As a result, the overall consumption of petroleum has leveled off since the Great Recession in the late 2000's and forecasts predict that the consumption of petroleum in the United States may begin to decrease—driving the price of petroleum even lower⁵. While there may be several options to limit the need of a liquid transportation fuel, the chemical industry still needs an abundant source of carbon to produce commodity chemicals and consumer goods. In fact, approximately 7% of a barrel of petroleum is not consumed as fuel, but is processed into chemicals such as ethylene, propylene, benzene, toluene, and lubricants⁶. Thus, biomass can play a significant role in producing chemicals and limiting the environmental concerns of petroleum^{7,8}.

To utilize biomass for renewable chemicals, however, the chemical industry needs to invent a host of new technologies. In addition to adapting pretreatment and separation processes to handle novel feedstocks and products, catalysts need to be developed that can perform various reactions while withstanding unique reaction conditions. For years, the majority of catalysis research and development has focused on gas phase reactions with petroleum-derived feedstocks. Typically, feedstocks derived from fossil sources have high volatility and low oxygen content. Biomass-derived feedstocks, on the other hand, usually consist of large, highly polar molecules with a high oxygen to carbon ratio. Therefore, if biomass is going to be used to supplant unsustainable fossil-derived chemicals, catalyst researchers in industry and academia need to develop catalysts that are able to operate in liquids, preferably water, and catalyze the removal of oxygen^{2–4}.

1.2 Glycerol as a Building Block Molecule

In 2004, the United States Department of Energy issued a study identifying the top value-added products derived from biomass, which can technically and economically produce fuels and chemicals from biomass in an integrated bio-refinery⁹. One of the

building block molecules identified in that study was glycerol, a highly water-soluble molecule with a carbon to oxygen ratio of unity. In addition to its versatility, glycerol was highlighted in the DOE study because it is produced as a waste product of biodiesel production. Biodiesel has been a commonly used transportation fuel in Europe since 1992, but in the early 2000's legislation in both the EU and the US caused a rapid increase in the production of biodiesel, which flooded the market with cheap, readily available glycerol¹⁰. As a result, a number of researchers are investigating glycerol as a chemical feedstock.

Glycerol is easily transformed into a number of chemicals including dihydroxyacetone, glycidol, glyceric acid, and propionic acid through either enzymatic or catalytic routes^{9,11–13}. In addition, glycerol can also undergo a process called aqueous phase reforming (APR) to produce H_2^{14} . Glycerol can also be processed through catalytic routes to produce two chemical products from the hydrogenolysis glycerol: 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO). The market for 1,2-PDO is already well-established because it is currently used directly as a food additive and antifreeze as well as in the production of polyester resins, liquid detergents, and pharmaceuticals¹⁵. Currently, 1,2-PDO is produced via the hydration of propylene oxide. The commercial production of 1,3-PDO by Shell currently utilizes ethylene oxide as a feedstock, which is derived from fossil sources. A more renewable route to obtain 1,3-PDO has recently been commercialized by DuPont and involves a fermentation route of glucose or glycerol with a recombinant microorganism¹². The production of 1,3-PDO using these processes, has increased recently due to the demand of polytrimethylene terephthalate or PPT polymer, which is comprised of 1,3-PDO and terephthalic acid. It would be more advantageous however, to explore a production route for both 1,2-PDO and 1,3-PDO involving a continuous process using a heterogeneous catalysts and a renewable feedstock.

1.3 Bimetallic Catalysts

Nanoparticles of transition metals supported on carbon or metal oxide carriers are commonly used to catalyze hydrogenolysis reactions because they readily dissociate H₂. Promotion of a transition metal catalyst with a second metal can sometimes lead to a higher rate of reaction and a higher selectivity to the desired product, thus increasing the effectiveness of the material^{16–18}. When rates, selectivies, or catalytic properties are different on the bimetallic material compared to a physical mixture of two monometallic catalysts, it indicates the combination of the two metals produced a unique catalyst.

The structure of the bimetallic nanoparticles and the relative orientation of the two metals within the nanoparticles also strongly influence the catalytic performance¹⁹. The structure of bimetallic catalysts is highly dependent on the metals used and the resulting structure has been shown to change under the environment to which the catalyst is subjected, thus increasing the complexity of these materials further^{20–22}.

The main influences on catalysis that adding a second metal to metal nanoparticles can be classified into geometric effects and electronic effects. Geometric effects occur when both metals are present on the surface of the nanoparticle, but the second metal is relatively inert compared to the catalytic metal. An example of a geometric effect is the addition of Cu to Ni catalysts for the isomerization of n-alkanes. Over the monometallic Ni catalyst the rate of dehydrogenation, which leads to isomerization products, is approximately the same as the rate of C-C bond cleavage reactions, which leads to short chain n-alkanes. Thus, when the isomerization of n-alkanes is performed over a Ni catalyst, high selectivity to undesired, short chain alkanes will be obtained because of the high rate of C-C bond cleavage. When Cu is added to the catalyst in increasing amounts, however, Figure 1.1 shows that the rate of C-C bond cleavage in ethane decreased whereas the rate of dehydrogenation of cyclohexane was unaffected. In those examples, the role of Cu was to dilute Ni ensembles that catalyze C-C bond activation, which require a group of 4-6 Ni atoms. The rate of dehydrogenation was relatively unaffected because the reaction only requires 1 or 2 Ni atoms. Therefore, even though Cu is relatively inert at the conditions of n-alkane isomerization, the addition of Cu changes the geometry of the active ensembles on the surface of the material and changes the catalytic properties²³.

Electronic (or ligand) effects arise when the addition of the second metal directly changes the electronic properties of the catalytic surface. An understanding of this effect is typically explained using the d-band model. Briefly, the d-band model relates the density of states or the energy of d orbitals to the Fermi level for a given material. The density of states above or below the Fermi level affects the strength of the interaction between the metal and an adsorbate. The addition of a second metal can change the d-band character of the base metal through an electronic interaction by changing the density of states near the Fermi level. For example, the energy of adsorption of oxygen or hydrogen onto Pt changes linearly with the d-band character of the promoting metal²⁴. In this situation, unlike with geometric effects, the promoting metal does not necessarily have to be on the surface of the catalyst in order to produce an electronic effect.



Figure 1.1: Activities of Ni-Cu catalysts for the hydrogenolysis of ethane to methane (C-C bond activation) and the dehydrogenation of cyclohexane to benzene²⁵.

Another influence that adding a second metal to metal nanoparticles can have on catalysis is formation of a bifunctional material. Bifunctional heterogeneous catalysts, whereby two catalytic functions exist in close proximity with one another, are typically comprised of a metal supported on a metal oxide carrier. A classic example of this is the Pt/Al₂O₃ catalyst for the isomerization of n-alkanes. The Pt provides the metal function that catalyzes the dehydrogenation of an n-alkane to form an n-alkene, which then migrates to an acid site on the Al₂O₃ support where it is rearranged to form a branched hydrocarbon.

In the final step of the reaction, the isoalkene is hydrogenated by the metallic Pt sites to form the final product²⁶. Examples of bifunctional catalysts consisting of two transition metals, however, are limited in the literature.

1.4 Selective Hydrogenolysis of Primary C-O bonds in Glycerol over Bimetallic Catalysts

To obtain 1,2-PDO from glycerol, primary (or terminal) C-O bonds need to be selectivity activated without catalyzing C-C bond cleavage. Monometallic Ru catalysts have been identified as active materials for the hydrogenolysis of glycerol at neutral pH. In fact, glycerol hydrogenolysis over Ru was faster than over Pt, but it is well known that Ru catalysts have a high rate of C-C bond activation, which leads to formation of ethylene glycol rather than more valuable 1,2-PDO, and produces a significant level of methane²⁷. Therefore, a large body of research in the literature attempts to find metals that can promote the selectivity of glycerol hydrogenolysis to 1,2-PDO over Ru based catalysts.

Maris et al. used several reaction probes to study glycerol hydrogenolysis over Ru-Pt and Ru-Au bimetallic catalysts supported on activated carbon²⁸. Even though in situ Xray absorption spectroscopy (XAS) and post-mortem transmission electron microscopy revealed that Ru-Pt bimetallic nanoparticles were formed on the carbon support and remained stable under reaction conditions (473 K in 0.8 M aqueous NaOH saturated in 4 MPa of H₂) results from glycerol hydrogenolysis were similar over Ru-Pt compared to a monometallic Ru catalyst. Using ethane hydrogenolysis as a probe reaction to measure surface Ru, it was shown that Au decorated Ru nanoparticles, which may have broken up Ru ensembles, but hydrogenolysis results over Au-Ru were also similar to the Ru catalyst. In addition, characterization showed that Au appeared to segregate off the Ru nanoparticles under glycerol hydrogenolysis conditions²⁸.

Conversely, Li et al. demonstrated that the addition of Fe to Ru nanoparticles supported on carbon nanotubes (CNT) increased the rate of glycerol hydrogenolysis at 473 K^{29} . Since, both Fe-oxide and Fe-metal diffraction peaks were observed by X-ray diffraction, it was thought that the addition of Fe to Ru on CNT formed Ru-Fe bimetallic nanoparticles with Fe-oxide clusters sitting at the interface of the bimetallic nanoparticles and the support²⁹. By adjusting the Ru/Fe atomic ratio used in the synthesis, the turnover frequency (TOF) of glycerol hydrogenolysis obtained with a Ru/Fe ratio of 2 was more than 200% greater than that measured over the monometallic Ru catalyst. In that work, the TOF was normalized to the number of Ru surface sites counted using an O₂-H₂ titration method²⁹. At the expense of a higher TOF, however, the selectivity to 1,2-PDO and ethylene glycol decreased. In addition to increasing catalyst activity, promotion of Ru with Fe also increased catalyst stability. In fact, the level of conversion or selectivity was barely unchanged after 5 uses of the catalysts, whereas the monometallic Ru catalyst lost approximately 25% of its activity after 5 reactions with the same batch of catalyst. Based on the results from this work it was thought that the Fe-oxides at the interface of the support prevented sintering of Ru, but it was unclear what caused the increase in TOF²⁹.

It is possible that excessive activation of C-C bonds by large Ru ensembles may lead to the formation of C_xH_y fragments strongly held to the surface, which block active sites and cause deactivation of the catalysts. Therefore, the addition of Fe to Ru, as reported by Li et al. to improve stability, may have broken up Ru ensembles preventing the formation of adsorbed C_xH_y fragments.

Both Salciccioli et al.³⁰ and Barbelli et al.³¹ highlighted the benefit of using a Pt-Ni bimetallic catalyst to selectively activate primary C-O bonds in ethylene glycol and glycerol, respectively. Barbelli et al. observed a selectivity to 1,2-PDO as high as approximately 70% in the liquid phase products of glycerol APR using Pt-Ni nanoparticles supported on alumina modified with Ce and Zr, but the majority of the product selectivity consisted of gas phase H₂ and CO_2^{31} . An extensive investigation by Salciccioli et al. using quantum chemical calculations and isotopic labeling experiments evaluated the mechanism of ethylene glycol decomposition over Pt-Ni catalysts³⁰. In that work, they observed that the addition of Ni lowered the energy to perform the initial dehydrogenation at the O-H and C-H bonds of ethylene glycol compared to the monometallic Pt catalyst, which explained the higher rate of ethylene glycol decomposition³⁰. The lower energy path on the Pt-Ni catalyst was ascribed to a change in the binding energy of oxygen, which was calculated to be 0.8 eV stronger on Pt-Ni compared to Pt. Thus the Pt-Ni catalyst may be a good candidate to obtain a high selectivity of 1,2-PDO from glycerol, but to the best of our knowledge no work in the literature currently focuses on increasing 1,2-PDO yield using a Pt-Ni catalyst.

1.5 Aqueous Phase Reforming of Glycerol over Bimetallic Catalyst Consisting of Platinum and an Early Transition Metal

In the early 2000's, Dumesic and co-workers began using supported platinum group metals to catalyze the APR of biomass derived molecules into H_2 and CO_2 , which could be

used as an alternative production method for H_2^{14} . Within the next couple of years, several monometallic and bimetallic catalysts consisting of transition group metals were developed to reform glycerol^{32–34}. Researchers observed that when Pt nanoparticles supported on activated carbon were promoted by Re or Mo, the rate of glycerol APR increased by an order of magnitude compared to monometallic Pt. Based on the liquid phase products, it appears that the bimetallic catalysts more selectively activated the secondary C-O bonds in glycerol^{35–37}.

Operando XAS of a carbon-supported Pt-Mo bimetallic catalyst revealed that the catalyst consisted of a Pt core with a MoO_x rich surface, but related density functional theory (DFT) calculations suggested that the thermodynamically stable nanoparticles consist of a Pt metal shell around a metallic Mo core³⁸. The inconsistency between the DFT and the experimentally observed result arose because the actual catalytic nanoparticles were synthesized from the co-reduction of PtO_x and MoO_x . Platinum oxides are easily reduced by H_2 at temperatures as low as 573 K, but the highly oxophilic Mo does not reduce until higher temperatures. Therefore, the Pt reduces to metal prior to the partial reduction of Mo. The resulting catalyst contained Pt metal nanoparticles with MoO_x covering the surface even though this configuration was not the most thermodynamically stable. In fact, CO chemisorption revealed that the surface was only 25% Pt with the rest covered by Mo. In addition, XAS showed that the Pt-Pt coordination number was very high and the Mo-Pt coordination number was larger than the Mo-Mo coordination number, which further supports the model that Pt was in the core and Mo was on the surface. This study also used X-ray photoelectron spectroscopy (XPS) to show that Mo was present in a range of oxidation states, even after reduction at 573 K in an ex situ cell. After reduction, Mo was present as Mo^{6+} , Mo^{4+} , as well as an oxidation state that the authors assigned to a Pt_3Mo species³⁸.

When Mo was added to the Pt based catalyst, the rate of APR of glycerol increased as much as 4 times³⁹. In addition, the TOF of H_2 production was higher over the Pt-Mo/C catalyst compared to the Pt/C catalyst. The molar ratio of CO_2 to CH_4 in the gas phase was similar on both catalysts in the range of about 3 to 9 depending on the conversion, which was never higher than 40%. One explanation for the higher rate of reforming as well as the higher rate of H_2 production was that the Pt-Mo/C catalyst had a lower binding energy of CO, which was supported by DFT calculations. The DFT calculations also suggested that the Pt-Mo/C also had increased rates of dehydrogenation and C-O bond activation compared to Pt. In addition, operando XAS of the Pt/C catalyst revealed that CO was the most abundant intermediate on the surface of the catalyst, but the gas phase products contained trace levels of CO. It was suggested that the high concentrations of water under APR conditions increased the rate of the water gas shift reaction (WGS) substantially. It was confirmed that the WGS reaction was indeed faster on the Pt-Mo/C catalyst than Pt/C^{40} . In the liquid phase, products arising from C-O bond cleavage (hydroxyacetone, propylene glycol, 1- and 2-propanol, acetone, propanal, ethanol, and acetaldehyde) as well as C-C bond cleavage (ethylene glycol, methanol) were detected. Therefore, at the conditions used in this work both the monometallic and the bimetallic catalyst activated C-C and C-O bonds. Even though the Pt-Mo/C catalyst had a higher rate of glycerol conversion, approximately 80-90% of the liquid phase products were a result of C-O bond

breaking on the Pt-Mo/C catalysts compared to 60-80% on the Pt/C catalyst. The difference in C-O and C-C bond breaking selectivity was even more evident below 0.5% conversion. This reveals that the addition of Mo shifted the selectivity towards the removal of oxygen.

Addition of Re to Pt also increased the rate of APR, up to 5 times higher than the Pt catalyst, but it actually lowered the selectivity to $H_2^{35,37,41-50}$. Evidently, the addition of Re or Mo to Pt increases the rate of the C-O bond cleavage, which leads to unsaturated hydrocarbons that consume $H_2^{41,42,45,47}$. In fact, results from NH₃ temperature programed desorption (TPD) and infrared spectroscopy of adsorbed pyridine indicated that Brønsted acid sites are present on the Pt-Re bimetallic catalyst^{41,42,45}. The increase in area of the NH₃ desorption peak and the absorption mode of pyridinium ion correlated with increasing Re content^{42,45}. However, in these works it was suggested that a steam treatment was required to activate the Brønsted acid site. Fu et al. also observed that the Pt-Re bimetallic catalyst was less active for the APR of 1-propanol compared 2-propanol, 1,2-propanediol, or hydroxyacetone⁴⁷ indicating that the Brønsted acid more readily activates secondary C-O bonds, rather than primary C-O bonds, which is consistent with carbenium ion chemistry⁵¹. The addition of base also increased the selectivity of H₂ slightly and lowered the selectivity to liquid alkanes indicating that the added base neutralized acid sites, which lead to a lower rate of C-O bond activation³⁷.

Characterization using X-ray absorption near edge structure $(XANES)^{45}$ and $XPS^{41,42,50}$ revealed that the Re was present as ReO_x on the surface of the catalyst, and that the surface was actually enriched in Re when the carbon-supported catalyst was reduced at temperatures lower than 723 K⁴⁵. After the catalyst was reduced at temperatures greater

than 723 K the oxidation state of Pt or Re did not change, and they both had an oxidation state of zero⁴⁵.

It was also observed that the addition of Re to Pt increased the rate of the WGS reaction substantially in the presence of steam or liquid water^{35–37,43–45,52}. Both stripping voltammetry and ATR-IR indicated that the addition of Re lowers the binding energy CO facilitating WGS^{42,45}. It was also suggested that strong oxophilicity of Re provides a site that readily dissociates water and creates an *OH intermediate on the surface^{35,45}. When water was not present, the CO binding energy on the Pt-Re catalyst was very strong under reducing conditions, but the binding of CO weakened when the catalyst was subjected to a steam treatment more closely resembling APR conditions⁴².

Using acetaldehyde decomposition as probe reaction for C-C bond cleavage, Ciftci et al. observed that Re promoted the rate of acetaldehyde decomposition^{44–46}. Therefore, the addition of Re increased the rate of WGS, C-O bond activation, and C-C bond activation, which accounts for the substantial increase in the rate of APR. While the rate of WGS and C-C bond activation increased upon the promotion of Pt by Re, which benefit the H₂ selectivity of APR, it appears that Re also promoted the rate of C-O bond activation more than C-C cleavage, which led to a lower H₂ selectivity⁴⁴. Therefore, the Pt-Re catalyst might be an ideal catalyst to reform oxygenated biomass to alkanes, but because of the high rate of C-O activation it is not the ideal catalyst to selectively produce H_2^{48} .

1.6 Selective Hydrogenolysis of Secondary C-O bonds over Bimetallic Catalysts

Supported platinum group metals were also being investigated for the selective hydrogenolysis of glycerol during the late 1900's and early 2000's^{27,28,53,54}.

Hydrogenolysis reactions are performed in high pressures of H_2 , but at temperatures much lower than APR since it is desirable to cleave bonds selectively to produce molecules like 1,2-PDO. In Scheme 1.1, the difference between these two classes of reactions and the resulting products is depicted, using glycerol as an example.

Concurrent with APR studies that hypothesized the addition of Re or Mo to Pt based catalysts formed produced Brønsted acid sites, it was observed that several catalysts consisting of a platinum-group-metal and an early transition metal were able to selectively activate the secondary C-O bond in glycerol to produce 1,3-PDO. In most works studying the hydrogenolysis of glycerol over monometallic catalysts the major product was 1,2-PDO^{13,27,55}, however, Kuraska et al. were the first to obtain a selectivity to 1,3-PDO greater than 10% from glycerol hydrogenolysis using a Pt/WO₃/ZrO₂ catalyst⁵⁶. In that work, 1,3dimethyl-2-imidazolidinone was used as the solvent, which is costly and environmentally unfriendly. Using a Rh-Re bimetallic catalyst, Tomishige and co-authors demonstrated that a 1,3-PDO selectivity up to 28% could be obtained in liquid water at 393 K⁵⁷. In a subsequent work, a variety of oxophilic promoters were added to Rh and it was found that Re increased the conversion of glycerol over the Rh based catalyst far higher than Mo, W, Mn, V and Zr⁵⁸. The highest selectivity to 1,3-PDO was also obtained with a Rh-Re bimetallic catalyst, while Rh-Mo and Rh-W bimetallic catalysts achieved a higher conversion of glycerol than a monometallic Rh catalyst⁵⁸. Daniel et al. also reported that the addition of Re to Pt increased the rate of glycerol hydrogenolysis by over an order of magnitude and the selectivity to 1,3-PDO increased from below the detectable limit on Pt to as high as 34% at 20% conversion of glycerol on Pt-Re/C⁵⁹. X-ray absorption spectroscopy and TEM energy dispersive X-ray spectroscopy were used in that work to show bimetallic Pt-Re nanoparticles were formed. In fact, the reduction of Re was catalyzed by the presence of Pt. Under reducing conditions, XANES revealed that the oxidation state of Re in carbon-supported catalyst was +7, the same as the Re precursor used. But when Pt was present, a shift in the Re L_{III} edge indicated that the oxidation state of Re was approximately $+2^{59}$. The highest selectivity to 1,3-PDO from glycerol hydrogenolysis was obtained using an Ir-Re bimetallic catalyst by Nakagawa et al⁶⁰. At 63% conversion of glycerol at 393 K, 49% of the products were 1,3-PDO⁶⁰.

To obtain appreciable rates of glycerol hydrogenolysis over monometallic precious metal catalysts, reaction temperatures typically have to be 473 K or higher and the selectivity to 1,3-PDO is usually below 5%, depending on the metal. The addition of Re, however, increases the rate of glycerol hydrogenolysis substantially and shifts the selectivity from hydrogenolysis at predominantly primary C-O bonds in glycerol, forming 1,2-PDO, towards hydrogenolysis of a mixture of terminal C-O bonds and internal C-O bonds, which produces 1,3-PDO. In addition to Rh, Pt, and Ir, the promotion of other transition metals by Re has also been observed with Ru-Re^{61,62} and Pd-Re⁶³ bimetallic systems. The selectivities to 1,3-PDO reached only about 10% on the Ru-Re and Pd-Re systems and the rates of glycerol hydrogenolysis were substantially slower on those systems compared to the Rh-Re, Pt-Re, and Ir-Re systems.



Scheme 1.1: The common conditions and desired products for glycerol APR and glycerol hydrogenolysis.

Extensive characterization of the Re bimetallic catalysts with XAS and XPS revealed interesting information about the oxidation state of the Re component of the catalyst in the Rh-Re^{64,65}, Pt-Re⁵⁹, and Ir-Re⁶⁶ systems. After synthesis of the Re based catalysts, which entailed a reduction or a calcination step at temperatures above 723 K, the Rh, Pt, or Ir component of the catalyst was always observed to be in the metallic state. Interestingly, the Re component of the catalyst was not completely reduced. On a silicasupported Rh-Re catalyst, Koso et al. measured the average oxidation of Re to be approximately 2+ using XANES⁶⁴. Daniel et al. also measured an average oxidation state of 2+ for Re on carbon-supported Pt-Re nanoparticles⁵⁹. Amada et al. used XAS and XPS to show that the oxidation of Re in Ir-Re catalyst was also approximately 2+⁶⁶. In all of these works it was demonstrated that the platinum group metal was always present in the metallic state and the presence of the platinum group metal was required to partially reduce Re. In addition, the binding energy of the metallic Pt was shifted slightly higher when Pt-Re bimetallic nanoparticles were formed^{59,67}. Reduction of rhenium in a monometallic Re catalyst does not occur until temperatures of approximately 573 K since the Re species
cannot dissociate H₂ at low temperatures^{59,64}. When a platinum group metal and Re form bimetallic clusters, however, the platinum group metal catalyzes the reduction of Re by dissociating H₂. Therefore, the Re is partially reduced at temperatures around 373 K. Interestingly, characterization of Pt-Re nanoparticles revealed that the Re component of the catalyst readily oxidizes after exposure to air after being removed from a reducing environment⁵⁹. Thus, an in situ reduction step is typically required prior to reaction to avoid leaching of highly oxidized Re. Although the extent of Re reduction increases at elevated temperatures^{64,66}, Koso et al. reported that Re never completely reduced on a Rh-Re catalyst even after reduction at 873 K⁶⁴. Chia et al. showed that as the in situ reduction temperature was increased, the rate of hydrogenolysis in liquid water at 393 K monotonically decreased⁶⁵.

Tungsten oxides were identified as another rate and selectivity promoter of Pt catalysts for glycerol hydrogenolysis to 1,3-PDO^{68–74}. For example, Li and co-authors have worked on a number of bimetallic catalysts containing Pt and heteropolyacids to obtain high yields of 1,3-PDO⁷². While the product selectivity appears to be similar on Pt-W bimetallic catalysts compared to the various Re-promoted bimetallic catalysts, the Pt-W system exhibits similar rates of hydrogenolysis at 473 K as the Re-promoted catalysts at 393 K, indicating the Re-based catalysts are far more active.

Researchers also discovered that catalysts consisting of a platinum group metal and an early transition metal were well suited to perform the ring opening of cyclic ether compounds that can easily be derived from moieties present in biomass sources. Koso et al. were the first to report very high rates of hydrogenolysis of tetrahydrofurfuryl alcohol (THFA) over Rh-Re bimetallic catalysts to produce 1,5-pentanediol with selectivies above 90% at 50% conversion of THFA⁷⁵. A paper by Chia et al. presented hydrogenolysis results from a host of cyclic ethers, in addition to THFA, and determined the Rh-Re bimetallic catalyst was very selective and highly active at ring opening hydrogenolysis in α , β -oxygen substituted substrates, some of which are depicted in Figure 1.2⁵¹. In fact, when the oxygen was removed from the α -carbon, the rates of hydrogenolysis decreased considerably⁵¹. The hydrogenolysis of THFA was also studied on Ir-Re⁷⁶, Ir-V⁷⁷, Ir-Mo⁷⁸, and Rh-Mo^{79,80} and all catalysts formed 1,5-PDO with selectivies over 90%. Interestingly, Xu et al. utilized a Pt/Co₂AlO₄ catalyst and was only able to obtain 1,5-PDO yields of approximately 20% from the hydrogenolysis of THFA⁸¹. Both Chia et al. and Koso et al also pointed out that the mechanism of cyclic ether ring-opening was very similar to the mechanism of glycerol hydrogenolysis to produce 1,3-PDO over the bimetallic catalysts consisting of a platinum group metal and an oxophilic metal, but a large disagreement over the mechanistic steps is present in the literature^{51,76}.



Figure 1.2: Selective hydrogenolysis of the secondary C-O bonds in several α , β -oxygen substituted substrates was observed over Rh-Re to produce the corresponding α , ω polyols

In addition to measuring the rates of hydrogenolysis of several different oxygenated substrates, NH₃-TPD on Rh-Re and quantum chemical calculations were also used to

propose a mechanism of hydrogenolysis. In the APR literature, it was reported that the addition of oxophilic promoters, like Mo and Re, created acidity on the catalytic surface that lead to high rates of C-O bond activation. Chia et al. used NH₃-TPD to show that acid sites were present on the Rh catalyst when Re was added as a promoter, but as expected the monometallic Rh catalyst did not possess any significant amount of acid sites⁵¹. Quantum chemical calculations described in Chia et al. also suggested that the deprotonation energy of hydroxyl groups bonded to the Re component of a Rh-Re bimetallic catalyst was on the order of the deprotonation energies measured for Brønsted acidic zeolites and heteropolyacids⁵¹. Furthermore, quantum chemical calculations suggest a number of hypothetical bimetallic systems consisting of a platinum group metal and an early transition metal that should have low deprotonation energies, with the Pt-Re system having the lowest (i.e. strongest calculated Brønsted acidity)⁸². Chia et al. also presented a correlation, depicted in Figure 1.3, between the formation energy of the proposed oxocarbenium ion intermediate and the rate of hydrogenolysis of the corresponding oxygenate. From the presence of acidity on the catalyst inferred by NH₃-TPD and calculated from DFT as well as the strong correlation in Figure 1.3. Chia et al. concluded that Brønsted acid sites are present on the Rh-Re bimetallic nanoparticles that are responsible for the selective and rapid activation of secondary C-O bonds in α,β -oxygen substituted substrates like glycerol⁵¹, THFA^{51,80}, and tetrahydrofuran-dimethanol⁸³.



Carbenium and Oxocarbenium Ion Formation Energy (kJ mol⁻¹)

Figure 1.3: The correlation between the ion formation energy of the oxocarbenium ion and the rate of hydrogenolysis of the corresponding oxygenate observed over a Rh-Re bimetallic catalyst at 393 K and 3.6 MPa of H_2 , which is consistent with a mechanism involving the acid catalyzed activation of C-O bonds⁵¹.

A mechanism involving a Brønsted acid site has also been suggested by Li and coauthors for glycerol hydrogenolysis over a Pt-W bimetallic catalyst. In their works, FTIR spectroscopy of adsorbed pyridine showed that bifunctional catalysts containing metallic Pt and a heteropolyacid, such as phosphotungstic acid or silicotungstic acid form Brønsted acid sites^{72,73}. By changing the heteropolyacid or by neutralizing the acid with alkali metal, they were able to obtain catalysts with different concentrations of Brønsted acid on the surface measured by integration of infrared spectra of adsorbed pyridine. They observed a strong correlation between the yield of 1,3-PDO and the number of Brønsted acid sites on the surface of the catalyst, shown in Figure 1.4, suggesting that Brønsted acid sites participated the formation of 1,3-PDO from glycerol^{72,73}. Interestingly, a correlation between the yield of 1,2-PDO and the number of Lewis acid sites was also observed (Figure 1.4)⁷².



Figure 1.4: The yield of 1,2-PDO and 1,3-PDO from the hydrogenolysis of glycerol at 453 K over bifunctional catalysts containing Pt and heteropolyacids⁷².

The mechanism involving the protolytic cleavage of a secondary C-O bond initiated by a Brønsted acid site will form an unsaturated intermediate following the initial step. Therefore, a hydrogenation step must follow the C-O bond activation to form the saturated alcohols^{51,82,83}. The platinum group metal should easily catalyze the hydrogenation of the hypothetical unsaturated intermediate. It has been shown in a number of works that intimate contact between the Brønsted acid site and the hydrogenating metal is required to obtain high rates of hydrogenolysis^{68,83}.

Another mechanism has been put forth in the literature by the Tomishige group^{76,84,85}. Contrary to the dehydration-hydrogenation mechanism discussed in the previous paragraph, the Tomishige group proposes a direct hydrogenolysis mechanism over a catalyst consisting of a platinum group metal and an early transition metal. In the first step of this mechanism, the terminal alcohol in glycerol or THFA preferentially adsorbs onto the Re component of the catalyst. Following adsorption, a hydride, which is produced from the heterolytic cleavage of hydrogen at the interface of Rh and Re, activates the secondary C-O. Therefore, Tomishige and co-authors argue that the strong, preferential adsorption of the oxygenated substrates onto the Re component of the catalyst explains the increase in rate and selectivity that is observed when early transition metals promote platinum group metals^{76,84,85}. The step involving the heterolytic cleavage of H₂ is supported by kinetic measurements showing that the rate is first order in H_2 for the hydrogenolysis of glycerol and THFA. With other substrates, however, Tomishige and co-authors have measured orders in H_2 that are less than unity or even zero^{86,87}. Thus, according to those works, the direct hydrogenolysis mechanism only applies to specific substrates. As a result, debate over the mechanism of hydrogenolysis on materials consisting of early and late transition group metals still persists.

1.7 Focus of this Work

Unraveling the roles of the metals and identifying how the reaction is altered upon formation of bimetallic particles rely upon extensive characterization of the catalytic surface as well as a detailed understanding of the reaction mechanism⁸⁸. In this dissertation, bimetallic catalysts were investigated for several biomass relevant reactions in liquid water including the hydrogenolysis of glycerol, the hydrolysis of propyl acetate, and the hydrogenation of unsaturated ketones and aldehydes. Chapter 2 of this dissertation discusses the geometric effects of the Ru-Cu bimetallic system for the selective hydrogenolysis of glycerol to 1,2-PDO. Chapters 3-5 investigates the bifunctional Pt-Re catalyst for glycerol hydrogenolysis to 1,3-PDO. An investigation of the possible electronic effects of the Pt-Re catalyst on the hydrogenation of ketones and aldehydes in liquid water is presented in Chapter 6.

The goals of the dissertation are to:

- 1. Understand the mechanism of glycerol hydrogenolysis over Ru-Cu
- 2. Confirm the presence of a Brønsted acid on Pt-Re
- 3. Measure the oxidation state of Re in the Pt-Re catalyst using XPS
- 4. Elucidate the mechanism of glycerol hydrogenolysis on Pt-Re in liquid water
- Interrogate any influence of Re on a Pt catalyst for the hydrogenation of C=C and C=O bonds.

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Chapter 2: Glycerol Hydrogenolysis over Bimetallic Ru-Cu/TiO₂

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2.1 Introduction

Biomass has been targeted as an alternative, renewable feedstock to fossil sources to produce cleaner, more sustainable fuels as well as commodity chemicals. The integration of biofuels and bio-chemicals within a so-called biorefinery can increase the viability of a bio-based economy¹. Glycerol, an important intermediate in the future bio-refinery, has been singled out by the US DOE and others as a candidate to produce a high number of valuable commodity chemicals and intermediates².

The increasing demand for biodiesel will produce a large amount of glycerol, as a byproduct, leading to a sharp decrease in the price of glycerol¹. Several studies to convert glycerol into higher value materials have been conducted in the past several years^{3–10}.

A viable application to utilize glycerol is the selective catalytic hydrogenolysis of glycerol to propylene glycol (1,2-propanediol, 1,2-PDO). Propylene glycol is an industrially important chemical and is extensively used in the production of polyester resins, functional fluids (antifreeze, deicing), paints and coatings, foods, pharmaceuticals and cosmetics. It is currently produced at an industrial scale using fossil-fuel-derived

propylene as the carbon feedstock⁹. Producing 1,2-PDO from glycerol hydrogenolysis is an attractive option because glycerol is a more sustainable feedstock compared to fossil sources.

Noble metal (Ru, Pt, Rh)^{7,11–18} and non-noble metal (Cu, Ni)^{19–25} catalysts have been tested for the hydrogenolysis of glycols. Among the transition metals, Ru has been shown to be the most active catalyst for hydrogenolysis; however, it has been well known to have high rates of C-C bond cleavage, which leads to excessive production of shorter chain polyols^{15,26,27}.

In recent a study, Wang et al. found that Ru exhibited a much higher activity in glycerol hydrogenolysis compared to Rh, Pt and Pd, all supported on $m-ZrO_2^{28}$. They also observed that the turnover rate increased three fold while there was a decrease in the selectivity to 1,2-PDO as the Ru particle size increased from 1.8 to 4.5 nm. The dependence of the rate of hydrogenolysis on the particle size and the surface catalyst structure has also been studied previously elsewhere^{29,30}.

In another study, Feng et al. evaluated Ru catalysts supported on various materials and they found that support and reduction temperature can influence the Ru particle size as well as the catalytic performance³¹. Among the supports tested, TiO₂ created the smallest and most stable Ru particles, which lead to the highest conversion of glycerol.

Copper-based catalysts supported on different metal oxides such as Al₂O₃, Cr₂O₃, ZnO, and SiO₂ among others, have also been widely studied for glycerol hydrogenolysis^{3,19–24,32,33}. Copper is known to have low rates of C-C bond cleavage while still exhibiting high rates of C-O bond cleavage in hydrogenolysis reactions³⁴. Therefore,

when Cu is used to catalyze the hydrogenolysis of glycerol it leads to a high selectivity of 1,2-PDO and limits the excessive C-C bond cleavage that causes the formation of undesired products. However, it has been observed that Cu catalysts exhibit low activity and high amounts of particle agglomeration during reaction^{28,29}. Recently, copper catalysts have been modified by $B_2O_3^{22}$ and $Ga_2O_3^{35}$ in attempt to obtain better dispersion and stability.

Bimetallic Ru-Cu catalysts have been studied extensively in the past several decades for a variety of applications^{5,36–40}. Bimetallic Ru-Cu nanoparticles supported on silica were used to catalyze ethane hydrogenolysis and showed a significant decrease in activity as the percentage of Cu increased compared to monometallic ruthenium catalyst. The researchers suggested that Cu at the surface of the particles has a significantly lower rate of C-C bond breaking than Ru^{39,41}. Moreover, Montassier and co-authors suggested that Cu metal has a high adsorption capacity for water and alcohols due to its electrophilicity and this adsorption leads to a weakening of the H-O or C-O bond⁴². This propensity for adsorbing water and alcohols might be enhanced when copper is associated with noble metals or metals with a lower d orbital electron occupancy, which can accept electrons from Cu leading to an increase in the Cu atom's electrophilicity.

Supported Ru-Cu bimetallic catalysts have also been applied to hydrogenolysis of glycerol. Jiang et al. employed Ru-Cu bimetallic nanoparticles supported on clay with the aid of ionic liquids³⁷. A catalyst with a Cu:Ru molar ratio of 1:3 achieved 100% conversion of glycerol and 85% yield of 1,2-PDO at 503 K with a H₂ pressure of 8 MPa after 18 h. More recently, 100% conversion of glycerol and 78.5% yield of 1,2-PDO was found with

a catalyst that had a Cu:Ru molar ratio of 1:10 at 453 K and 8 MPa of H_2 after 24 h of reaction⁵.

Bimetallic Ru-Cu catalysts have been shown to exhibit good performance and selectivity to 1,2-PDO for glycerol hydrogenolysis. Unfortunately, the reaction rates and turnover frequencies for Ru-Cu catalyst have not been adequately described in the literature, which prevents elucidation of fundamental structure-function relationships associated with this class of material. Thus, in this work, a series of TiO₂ supported Ru-Cu bimetallic catalysts with different Cu/Ru molar ratios were prepared and their turnover frequencies were evaluated for the hydrogenolysis of glycerol. Furthermore, H₂ chemisorption, X-ray diffraction (XRD), scanning transmission electron microscopy (STEM/EDS) and X-ray photoelectron spectroscopy (XPS) were used to characterize the metal components of the catalysts.

2.2 Experimental Methods

2.2.1 Catalyst preparation

The support, TiO₂ (S_{BET}: 50 m² g⁻¹), was obtained from Evonik-Degussa GmbH-P25. The precursors used for ruthenium and copper were Ru(NO)(NO₃)₃ in dilute nitric acid (Sigma-Aldrich) and Cu(NO₃)₂·3H₂O (Alfa Aesar), respectively. The catalysts were prepared by successive incipient wetness impregnations of Ru and Cu. The appropriate amount of precursor was dissolved in distilled, deionized water and the solution was introduced to the support using a ratio of 0.65 g of solution per gram of TiO₂. The solutions of Ru precursor were added dropwise with thorough mixing between additions. After saturating the pores, the material was dried at 393 K for 2 h, and then the next impregnation with Cu precursor solution was performed. Catalysts with different Cu/Ru weight ratios (1:2, 1:1, 2:1 and 4:1) were prepared, as well as their monometallic counterparts, 2.5 wt% Ru and 2.5 wt% Cu.

The catalysts were reduced in H₂ (GTS Welco, 5.0 UHP) flowing at 100 cm³ min⁻¹ at 573 K for 4 h with a heating rate of 5 K min⁻¹ before reactions were performed. In addition, the 2.5Ru/TiO₂ and 2.5Ru-2.5Cu/TiO₂ catalysts were reduced at two different temperatures (493 and 573 K) to evaluate the influence of reduction temperature on the dispersion of the metal particles supported on TiO₂. The catalysts were identified by their weight percentages of metal, such as: 2.5Ru/TiO₂; 5Ru-2.5Cu/TiO₂; 2.5Ru-2.5Cu/TiO₂; 2.5Ru-5Cu/TiO₂; 2.5Ru-10Cu/TiO₂ and 2.5Cu/TiO₂.

2.2.2 Catalyst characterization

Hydrogen chemisorption was performed in a Micromeritics ASAP 2020 automated adsorption analyzer. The samples were reduced at 493 or 573 K under flowing H₂ for 60 min, and then outgassed under vacuum at 493 or 573 K for 60 min. After this, the catalysts were cooled to 308 K and evacuated again for 60 min followed by analysis at 308 K. The total amount of H₂ adsorbed was calculated by extrapolating the hydrogen uptake to zero pressure, assuming a stoichiometry H/Ru_{surf} equal to unity. The mean particle size was calculated from the metal dispersion D, assuming spherical particles, where the equation d (nm) = v/D was applied (where v =1.32)⁴³.

The X-Ray Diffraction (XRD) patterns were obtained using a PANalytical X'Pert Pro MPD (Multi-Purpose Diffractometer) instrument equipped with a Cu X-ray (λ K α =1.54 Å) tube source. The XRD patterns were collected with 2 θ spanning from 20° to 90° with integration times of 30 s step⁻¹ and a step size of 0.05°. The spent catalysts were also analyzed after being washed with distilled, deionized water and filtered with 0.45µm pore sized filter paper, then dried overnight at 393 K.

The metal particle size was assessed by scanning transmission electron microscopy (STEM) utilizing a JEOL 2010F transmission electron microscope operating at 200 kV, in high-angle annular dark field (HAADF) mode, equipped with an energy dispersive X-ray analysis spectrometer (EDS). The samples were dispersed in ethanol and mounted on either a Cu mesh grid (monometallic Ru catalyst) or a gold mesh grid (rest of the catalysts).

The XPS analysis was performed with a Thermo ESCAlab 250S Spectrometer at the Virginia Commonwealth University (VCU) in Richmond, Virginia, employing a focused monochromatic Al K α X-ray (1486.6 eV) source, running with a pass energy of 20 eV and a 95 mm field emission gun. In this work, the peak of Ti (2p_{3/2}) = 459.4 eV was taken as a reference instead of the adventitious carbon peak because of the superposition of the C 1s and Ru 3d peaks around 285 eV.

2.2.3 Hydrogenolysis of glycerol

Reactions were carried out with 50 mL of a 20 wt% aqueous glycerol (Acros, 99.6% purity) solution in a 100 mL stainless steel autoclave (Parr Instruments). The previously reduced catalyst was loaded into the reactor with the solution. The reactor was sealed and flushed with flowing H₂ at atmospheric pressure and room temperature for 25 min to remove any air in the headspace. Then, the reactor was pressurized to 2.5 MPa with H₂ and heated to the reaction temperature of 473 K while stirring at 500 rpm. Samples were taken periodically (1, 2, and 3 h) through a sampling loop during the reaction. At the end of the

reaction (12 h), the reactor was allowed to cool down to room temperature and the liquid sample was collected. All samples were filtered with a 0.2 μm pore size filter and analyzed using a high performance liquid chromatograph (HPLC - Alliance) equipped with an Aminex HPX-87H (Bio Rad) column and a refractive index detector. The HPLC column was maintained at 318 K, with a mobile phase of 5 mM H₂SO₄ flowing at 0.5 mL min⁻¹. The liquid-phase products observed were 1,2-propanediol, ethylene glycol, 1,3-propanediol, lactic acid, ethanol, 1-propanol, and 2-propanol.

The initial TOF and conversion were calculated using the following equations:

$$TOF(s^{-1}) = \frac{Amount of formed products (mol)}{Total surface metal atoms (mol) \cdot Reaction time (s)}$$

Liquid product based conversion $(s^{-1}) = \frac{Amount of formed products (mol)}{Initial amount of glycerol (mol)} \cdot 100$

 $\frac{Glycerol \text{based conversion } (\text{s}^{-1}) =}{\frac{Initial \text{ amount of glycerol } (\text{mol}) - Final \text{ amount of glycerol } (\text{mol})}{Initial \text{ amount of glycerol } (\text{mol})} \bullet 100$

The initial TOF was based on the initial rate calculated at conversions lower than 20%. To compare rates at higher levels of conversion, a site-time yield (STY) based on hydrogen chemisorption has also been used.

2.3 Results and discussion

2.3.1 Catalyst characterization

The molar Cu/Ru ratio measured by XPS and wide area EDS for the catalysts used in this study are reported in Table 2.1. The nominal Cu/Ru atomic ratio of the bimetallic samples was always between the atomic ratio determined by XPS and wide area EDS (Table 2.1), suggesting that both methods provide self-consistent trends in metal composition. The $3d_{5/2}$ and $3d_{3/2}$ XPS peaks for the monometallic Ru catalyst were located at binding energies of 280.5 and 286.4 eV, respectively, whereas the $2p_{3/2}$ and $2p_{1/2}$ binding energies for the monometallic Cu catalyst were measured at 933.1 and 953.1 eV, respectively. As revealed in Table 2.1, the binding energies of both Ru and Cu in the bimetallic catalysts were similar to those of the monometallic catalysts and revealed no clear trend with composition, suggesting electron transfer between the two metals in the bimetallic catalysts was minimal.

Table 2.1: Characterization results from wide area EDS and XPS of catalysts reduced at 573 K.

Catalyst	Cu/Ru	Cu/Ru	Cu/Ru	Cu/Ru XPS Bi			ding Energies		
Catalyst	(mol/mol)	(mol/mol)	(mol/mol)		(eV)				
	Nominal	EDS	VDC	Ru	Ru	Cu	Cu		
	Nommai	ED3	лгэ	3d _{5/2}	3d _{3/2}	2p _{3/2}	2p _{1/2}		
$2.5 Ru/TiO_2$	-	-	-	280.5	286.4	-	-		
5Ru-2.5Cu/TiO ₂	0.8	1.0	0.8	281.0	286.1	933.2	953.2		
$2.5Ru-2.5Cu/TiO_2$	1.6	2.0	1.4	280.9	286.4	933.2	952.9		
$2.5Ru-5Cu/TiO_2$	3.2	4.3	1.7	281.1	286.2	933.5	953.5		
2.5Ru-10Cu/TiO ₂	6.4	6.4	3.4	281.0	286.4	933.9	953.7		
2.5Cu/TiO ₂	-	-	-	-	-	933.2	953.1		

Representative STEM images of the samples are provided in Figures 2.1 and 2.2.

Figure 2.1 shows images for the monometallic Ru and Cu catalysts along with their corresponding particle size distributions (PSDs) and Figure 2.2 presents STEM images of the bimetallic catalysts along with single particle EDS. Particle sizes from STEM as well as hydrogen uptake from H_2 chemisorption are shown in Table 2.2. The particle size for the monometallic Ru catalyst determined by H_2 chemisorption (4.2 nm) and the average particle size from STEM (1.8 nm) showed some difference, but good agreement was found

when results from chemisorption were compared with the surface average particle size (3.2 nm).

Catalyst ^a	H Uptake (µmol/gcat)	Ru dispersion ^b (H/Ru _{surf})	STEM particle diameter (nm)	Surface average diameter ^c (nm)
2.5Ru/TiO ₂	69	0.31	1.8	3.2
5Ru-2.5Cu/TiO ₂	118	0.28	3.1	4.3
$2.5Ru-2.5Cu/TiO_2$	43	0.21	2.1	3.2
2.5Ru-5Cu/TiO ₂	47	0.25	2.4	3.5
2.5Ru-10Cu/TiO ₂	27	0.21	2.7	3.7
2.5Cu/TiO ₂	-	-	1.7	2.1

Table 2.2: Results from H₂ chemisorption and STEM.

^aAll catalysts were reduced at 573 K.

^bDetermined by H₂ chemisorption.

^c Determined by STEM ($\Sigma d^3/\Sigma d^2$).

The hydrogen adsorption capacity per gram of catalyst (H_{ads}/g_{cat}) for each sample was determined by extrapolation of the high pressure, linear portion of the adsorption isotherm to zero pressure. The monometallic 2.5Ru/TiO₂ catalyst exhibited the highest H₂ chemisorption capacity followed by 5Ru-2.5Cu/TiO₂. As expected, the monometallic Cu sample had a negligible hydrogen adsorption capacity, but when Cu was mixed with Ru there was a slight decrease in H/Ru, likely the result of Cu deposition onto the Ru surface (Table 2.2). Presumably, this decrease in adsorption capacity is evidence for the formation of bimetallic ruthenium-copper particles with some portion of the Cu adsorbed on the surface of the Ru. This conclusion is also corroborated by single particle EDS analysis of the bimetallic catalysts which confirmed that small particles contain both Ru and Cu (Figure 2.2).



Figure 2.1: HAADF-STEM images with corresponding particle size distributions (PSD) for: (a) 2.5Ru/TiO₂, (b) 2.5Cu/TiO₂.

Sinfelt et al. studied the Ru-Cu system and found that the addition of 5% Cu to Ru was enough to decrease markedly the hydrogen chemisorption capacity by approximately 60% compared to monometallic Ru^{41} . Rouco et al. found that as the nominal Cu/Ru molar ratio of a Cu-Ru/SiO₂ catalyst was increased from 0 to 0.667, with the Ru weight percent held constant at 3%, the H/Ru ratio determined by H₂ chemisorption remained approximately constant³⁹. The authors suggested that either some of the hydrogen might be adsorbed on Cu, which is facilitated by spillover from surface Ru atoms, or the particle

size slightly decreased as more Cu was incorporated with Ru. Interesting behavior was also found with a series of Ru-Cu particles supported on high surface area graphite to which a low amount of Cu content was added; a higher Cu content led to higher dispersion even compared to monometallic Ru⁴⁴. In the current work, we observed the dispersions (H/Ru) of the 2.5Ru-2.5Cu/TiO₂, 2.5Ru-5Cu/TiO₂, and 2.5Ru-10Cu/TiO₂ were similar (Table 2.2), indicating that an increase in the Cu content in the sample did not suppress the chemisorption capacity of the Ru beyond that accomplished by adding a low level of Cu. We attribute these results to the formation of separated small clusters of exclusively Cu on samples that have high loadings of Cu. Single particle EDS and the number of particles with very light contrast suggest that samples with higher Cu/Ru molar ratio (Figure 2.2c and 2.2d) have more monometallic Cu particles than samples with lower Cu/Ru molar ratio. Furthermore, XRD analysis (Figure 2.3f and 2.3g) revealed that increasing the Cu content of the catalysts resulted in the formation of a crystalline Cu phase. The diffraction peaks at $2\theta = 43.2^{\circ}$, 50.4° and 74.5° corresponding to (111), (200) and (220) crystalline planes of copper, respectively, were observed for the fresh 2.5Ru-5Cu/TiO₂ and 2.5Ru-10Cu/TiO₂ catalyst (Figure 2.3f and 2.3g)⁴⁵. These peaks only appeared in catalysts that had a copper content greater than 5%.

		b
	Ē	
	B	Â
D	C	<u>5 nm</u>



EDS for (a)						EDS for (b)							
Particle	A	В	C	D	Е	F	Particle	A	В	С	D	Е	F
Ru (at%)	12	-	1.5	0.51	22	-	Ru (at%)	8.1	0.85	5.9	6.8	1.9	1.8
Cu (at%)	8.9	3.3	5.7	1.9	6.7	9.2	Cu (at%)	3.5	1.9	2.7	5.5	1.4	1.1
CuRu	0.78	241	3.8	3.9	0.31	<u></u>	Cu:Ru	0.43	2.2	0.46	0.81	0.70	0.63
EDS for (c)													
D 1 1	A	D	0	D	P	T	EDS for (d)		P	a	P	F	
Particle	A	В	С	D	E	F	EDS for (d) Particle	A	В	С	D	E	F
Particle Ru (at%)	A 0.36	B -	C -	D 3.0	E 3.5	F	EDS for (d) Particle Ru (at%)	A -	В 9.3	C -	D 3.0	E 2.1	F 1.3
Particle Ru (at%) Cu (at%)	A 0.36 0.49	B - 3.4	C - 1.1	D 3.0 5.8	E 3.5 7.3	F - 2.9	EDS for (d) Particle Ru (at%) Cu (at%)	A - 1.8	B 9.3 3.3	C - 5.4	D 3.0 2.0	E 2.1 3.4	F 1.3 2.7

5 nm

Figure 2.2: HAADF-STEM images with corresponding single particle EDS results for: (a) 5Ru-2.5Cu/TiO₂, (b) 2.5Ru-2.5Cu/TiO₂, (c) 2.5Ru-5Cu/TiO₂, (d) 2.5Ru-10Cu/TiO₂.

The XRD patterns of the bimetallic catalysts and of the blank support showed peaks associated with anatase and rutile phases of the TiO₂ crystalline domains (Figure 2.3)⁴⁶. The XRD patterns of all the fresh and spent samples did not show any peaks ascribed to Ru, presumably because of the high dispersion of the Ru particles. A high dispersion of Ru was confirmed by STEM, which revealed number average particle sizes smaller than 3.1 nm for all of the catalysts studied, as reported in Table 2.2.



Figure 2.3 X-ray diffraction patterns (a) TiO_2 , (b) $2.5Ru/TiO_2$, (c) $2.5Ru/TiO_2$ (spent), (d) $2.5Ru-2.5Cu/TiO_2$, (e) $2.5Ru-2.5Cu/TiO_2$ (spent) (f) $2.5Ru-5Cu/TiO_2$, (g) $2.5Ru-10Cu/TiO_2$. (All diffractograms are associated with fresh catalysts unless otherwise noted).

2.3.2 Effect of reduction temperature

The reduction temperature can influence the chemical interaction between noble metal and the support surface known as a strong metal-support interaction (SMSI). Tauster et al. found that at elevated reduction temperatures the amount of exposed Ru atoms supported on TiO₂ decreased, but not due to metal agglomeration⁴⁷. The reducibility of TiO₂ oxide is favored at elevated temperature. The authors found that the high reduction temperature of 773 K lead to the partial coverage of Ru metal particles by Ti₂O₃ species decreasing the number of Ru active sites compared to a catalyst reduced at 473 K⁴⁷.

In this work, 2.5Ru/TiO₂ and 2.5Ru-2.5Cu/TiO₂ catalysts were reduced at two different temperatures, 493 and 573 K, to determine if active surface sites were covered by Ti₂O₃ species. The lower temperature (493 K) was chosen based on previous TPR results which showed monometallic Ru can be reduced to Ru metal at around 490 K¹¹. Copper oxide also reduces to metallic Cu at temperatures around 450 K⁴⁴.

Table 2.3: Effect of reduction temperature on Ru dispersion and TOF for monometallic Ru and 2.5Ru-2.5Cu/TiO₂.

Catalyst	Ru dispersion ^a	Conversion ^b	Chemi. TOF ^c	Р	roduct s	electivity (%)	
5	(H/Ru _{surf})	(%)	(s^{-1})	1,2-PDO	EG	1,3-PDO	Others ^d
2.5Ru/TiO2 ^e	0.34	18.7	0.13	51	40	2	7
2.5Ru/TiO2 ^f	0.31	19.1	0.14	48	41	3	9
2.5Ru-2.5Cu/TiO2 ^e	0.21	9.6	0.11	68	23	0	9
$2.5 Ru - 2.5 Cu / Ti O_2^f$	0.21	9.7	0.11	69	25	0	6

Reaction conditions: 20 wt% gly solution, T = 473K; H₂ Pressure = 2.5 MPa; 0.6 g of catalyst Reaction time: 1h. All carbon balances were between 95 and 103%

^aDetermined by H₂ chemisorption.

^bBased on total liquid phase products. Conversions were the average of 3 experiments, with an error < 2%.

^cBased on total liquid phase products normalized to the H₂ chemisorption capacity.

^dOthers: 1-propanol, 2-propanol, ethanol, methanol, lactic acid.

^eReduced at 493K.

^fReduced at 573K.

As shown in Table 2.3, changing the reduction temperature within this range did not significantly alter either the H₂ chemisorption capacity or the catalytic activity. Also, the particle diameter measured by STEM was similar at both temperatures (493 and 573 K). Nevertheless, these results contrast those reported by Feng et al.³¹. They observed a decrease in the conversion of glycerol and an increase in particle size of Ru supported on TiO₂ with increasing catalyst reduction temperature from 473 to 573 K. The difference between our results and those of Feng et al. might be attributed to the slightly broader range in reduction temperature used by Feng et al. Additionally, Feng et al.³¹ and Tauster et al.⁴⁷ used RuCl₃ as precursor, while the Ru precursor used in this study was Ru(NO)(NO₃)_{3.}

2.3.3 Glycerol hydrogenolysis activity and selectivity

Table 2.4 summarizes the reaction results determined at low conversion for all of the catalysts used in this work. The carbon balance was based on total carbon accounted for in the liquid phase. No conversion was observed when a reaction was performed with blank TiO₂. As shown in Table 2.4, the presence of a metal catalyst was required to catalyze hydrogenolysis at this temperature. The addition of Cu metal to the Ru-based catalyst markedly enhanced the selectivity towards 1,2-PDO, despite the slight decrease in activity compared to monometallic Ru. The glycerol hydrogenolysis activities of the catalysts were measured by calculating the TOF based on both H_2 chemisorption uptake as well as the total number of metal surface atoms. Surface metal atoms counted by H₂ chemisorption are assumed to be associated with Ru, since Table 2.2 indicates a negligible hydrogen uptake on Cu. The number of total metal surface atoms (Ru + Cu) was estimated from the particle size measured by STEM and the total metal loading on the sample. The rate of glycerol hydrogenolysis, based on total metal surface atoms, decreased substantially as the Cu/Ru ratio increased. This is attributed to the substantial fraction of low activity monometallic Cu particles present with the bimetallic RuCu particles at higher Cu loadings. The monometallic Cu catalyst was the least active catalyst, as expected. In contrast, the normalized rate of glycerol hydrogenolysis based on total H₂ uptake did not change substantially as the Cu/Ru ratio increased (Table 2.4), consistent with the conclusion that high levels of Cu did not substantially block active Ru sites. The only exception in this

trend was the $5Ru-2.5Cu/TiO_2$ catalyst. The results also show that when the Cu/Ru ratio increased, the selectivity to 1,2-PDO increased from 48% in the case of monometallic Ru up to 97% for the 2.5Ru-10Cu/TiO₂ catalyst, at the expense of ethylene glycol production. It must also be noted that the 2.5Ru-10Cu/TiO₂ catalyst had approximately the same product selectivity as the monometallic Cu catalyst.

Catalyst	Time	Conversion ^a	Chemi.	Surf.	Product selectivity (%)			ty (%)
	(h)	(%)	TOF ^b	Met.				
			(s^{-1})	TOF ^c	1,2-	EG	1,3-	Others ^d
				(s^{-1})	PDO		PDO	
Blank	12	0.00	-	-	-	-	-	-
TiO ₂	12	< 1.0	-	-	-	-	-	-
$2.5 Ru/TiO_2$	1	19	0.14	0.13	48	41	3	9
5Ru-2.5Cu/TiO ₂	1	11	0.048	0.034	64	24	4	8
$2.5Ru-2.5Cu/TiO_2$	1	10	0.11	0.027	69	25	0	6
2.5Ru-5Cu/TiO ₂	1	8.6	0.091	0.015	74	21	0	6
2.5Ru-10Cu/TiO ₂	2	8.4	0.081	0.0050	96	3	0	2
2.5Cu/TiO ₂	12	13	-	0.0027	97	2	0	1
$2.5 Ru/TiO_2 +$	1	15	0.055	0.056	50	20	5	7
$2.5Cu/TiO_2$	1	15	0.055	0.056	38	30	3	/

Table 2.4: Catalyst performance in glycerol hydrogenolysis at low conversion.

*Reaction conditions: 20 wt% gly solution, T = 473 K; H_2 Pressure = 2.5 MPa; 0.6 g of catalyst.

All catalyst were reduced previously at 573K. All carbon balances were between 95 and 103%

^aBased on total liquid phase products. Conversions were the average of 3 experiments which had an error < 2%.

^bBased on total liquid phase products normalized to the H₂ chemisorption capacity. ^cBased on total liquid phase products normalized to surface metal atoms (Ru+Cu) evaluated from the inverse of the surface average particle size obtained by STEM. ^dOthers: 1-propanol, 2-propanol, ethanol, methanol, lactic acid

These results suggest that the role of Cu within these bimetallic particles is to dilute

the large Ru ensembles that are responsible for C-C bond cleavage that lead to ethylene

glycol production. However, the addition of copper does not seem to substantially decrease

the ability of Ru to carry out the cleavage of C-O bonds, which leads to the production of

1,2-PDO. As shown by Sinfelt et al., only small ensembles or perhaps single atoms of Ru are needed to catalyze C-O cleavage⁴¹. These results also suggest that Ru and Cu need to be atomically mixed within the catalyst in order to increase the selectivity to 1,2-PDO. A low selectivity to 1,2-PDO was observed when the monometallic Cu and Ru catalyst were physically mixed in the batch reactor.



Figure 2.4: Comparison of conversion, based on liquid phase products, and carbon balance from glycerol hydrogenolysis at 473 K over supported Ru, Cu, and Ru-Cu catalysts after 12 h of reaction. Conditions: 20 wt% gly solution, T = 473 K; H₂ Pressure = 2.5 MPa; 0.6 g of catalyst.

Figure 2.4 illustrates the conversion and 1,2-PDO selectivity after 12 h of reaction for monometallic Ru and the bimetallic catalysts. The 2.5Ru-2.5Cu/TiO₂ catalyst exhibited

the best performance in the hydrogenolysis of glycerol with 53.9 % conversion, 93.2% 1,2-PDO selectivity, and with a carbon balance of 95% after 12 h. Furthermore, among the bimetallic catalysts, 2.5Ru-2.5Cu/TiO₂ exhibited the highest initial TOF as reported in Table 2.4.

2.3.4 Deactivation and catalyst recycle

The conversion based on liquid phase products, the conversion based on glycerol, and the carbon balance for the monometallic Ru and bimetallic 2.5Ru-2.5Cu/TiO₂ over the course of the 12 h reaction is shown in Figure 2.5. After 1 h of reaction, the activity of the monometallic Ru catalyst was initially high (STY of 0.14 s⁻¹, Table 2.5), but as the reaction proceeded, the STY decreased substantially to 0.019 s⁻¹ after 12 h. In an analogous experiment with 2.5Ru-2.5Cu/TiO₂, the initial STY of the bimetallic catalyst after 1 h was 0.055 s⁻¹ and only slightly decreased 0.038 s⁻¹ after 12 h, indicating little deactivation with time on stream. Part of the decrease in the rate of liquid phase product evolution for monometallic Ru arises from the production of gas phase species from the difference between the conversion based on liquid phase products and the conversion based on glycerol. Gas phase products were not measured in this work, but as shown in Table 2.4, the monometallic Ru catalyst exhibited a high selectivity to ethylene glycol which is formed by C-C bond cleavage. Subsequent hydrogenolysis reactions involving C-C bond cleavage to species with high vapor pressures is likely and has been demonstrated by Maris and Davis ¹⁵. Nevertheless, the reaction profiles in Figure 2.5 still suggest that substantial deactivation of the monometallic Ru catalyst was occurring and could not be completely

accounted for by unmeasured gas phase products since the carbon balance was greater than 80% after 12 h of reaction.



Figure 2.5: Reaction profiles for glycerol hydrogenolysis at 473 K over supported 2.5Ru/TiO₂ and 2.5Ru-2.5Cu/TiO₂ catalysts.

The reusability of monometallic Ru catalyst and 2.5Ru-2.5Cu/TiO₂ was evaluated by recycling the catalyst and re-testing it under the same reaction conditions. After a 12 h reaction run, the spent catalyst was washed thoroughly with distilled, deionized water, filtered, and then dried at 393 K overnight. The results for two cycles are reported in Table 2.5. The mass of catalyst used in each reaction is listed in Table 2.5 since complete catalyst recovery was not achieved. The observed deactivation of the monometallic Ru catalyst during the reaction profile in Figure 2.5 was likely caused by adsorption of some unidentified carbon-containing species on the Ru sites because a simple washing step was sufficient to regenerate most of the active catalytic sites as shown in the recycle experiments in Table 2.5.

Catalyst	Cycle	Mass cat.	Time (h)	Conv. ^a (%)	Site- Time	Product selectivity (%)			
		(g)	(11)		Yield (s ⁻¹) ^b	1,2- PDO	E G	1,3- PDO	Others ^c
	Cycle I	0.608	1	19	0.14	48	41	3	9
2.5Ru/TiO ₂			12	31	0.019	57	15	14	14
	Cycle II	0.552	1	14	0.11	50	40	2	8
2 5Du	Cycle I	0.603	1	4.7	0.055	84	14	1	2
2.5Ku^2			12	39	0.038	90	6	1	3
2.3 Cu/ 1102	Cycle II	0.519	1	2.8	0.038	85	12	2	2

Table 2.5: Recycle experiments with 2.5Ru/TiO2 and 2.5Ru-Cu/TiO2 catalysts for glycerol hydrogenolysis

^{*}Reaction conditions: 20 wt% gly solution, T: 473 K; H₂ Pressure = 2.5 MPa. All carbon balances were between 95 and 105%. The spent catalyst was recovered by filtration with a 0.45 μ m pore membrane, washed with distilled, deionized water and dried at 393 K before recycle

^aBased on total liquid phase products.

^bBased on total liquid phase products normalized to the H₂ chemisorption capacity of the fresh catalyst

^cOthers: 1-propanol, 2-propanol, ethanol, ethanol, lactic acid.

^dThese experiments were performed in a 300 mL volume Parr reactor whereas all other experiments were performed in a 100 mL Parr reactor.

The $2.5Ru-2.5Cu/TiO_2$ catalyst also had a small decrease in the initial STY between

the two recycle runs (Table 2.5). Interestingly, the STY after 12 h with 2.5Ru-2.5Cu/TiO₂

was the same as that after 1 h of reaction in cycle II. The bimetallic catalyst apparently

does not suffer from deactivation by weakly adsorbed side products in the same manner as

the monometallic Ru catalyst.

We do not attribute the deactivation during the reaction profile of the monometallic Ru catalyst and 2.5Ru-2.5Cu/TiO₂, shown in Figure 2.5, to substantial particle growth because the XRD pattern for the spent catalysts (Figure 2.3c,e) did not show any Ru or Cu diffraction peaks, and STEM spent of 2.5Ru/TiO₂ revealed only a slight increase in the mean particle diameter. The fresh monometallic Ru catalyst had a mean particle size of 1.8 \pm 1.0 nm whereas that of the catalyst recovered after the recycle experiments was 3.4 \pm 1.8 nm. In fact, the reduction of initial STY after recycling (Table 2.5) can be attributed to the increase in particle size since the STY in Table 2.5 is based on the dispersion of the fresh catalyst evaluated by H₂ chemisorption.

2.4 Conclusions

The addition of Cu metal to a Ru-based catalyst markedly enhanced the selectivity towards 1,2-PDO. The hydrogenolysis rate on the Ru-Cu bimetallic catalysts, based on total metal atoms, was at least an order of magnitude lower than that on a monometallic Ru catalyst, whereas the rate based on H₂ chemisorption was only slightly lower. The role of Cu within these bimetallic particles most likely acts to dilute large Ru ensembles that are responsible for C-C bond cleavage that leads to ethylene glycol production instead of the desired 1,2-PDO. The presence of Cu also appears to inhibit the deactivation exhibited by monometallic Ru as the reaction progressed. Among all the catalysts, the 2.5Ru-2.5Cu/TiO₂ catalyst exhibited the best performance in the hydrogenolysis of glycerol.

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Chapter 3: Synthesis of Pt-Re Bimetallic Catalysts for Glycerol Hydrogenolysis

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3.1 Introduction

Interest in bimetallic catalysts consisting of a late transition metal such as Pt together with an oxophilic metal like Re has increased in recent years because of their potential application in several reactions relevant to the transformation of biomass-derived molecules to fuels and chemicals^{1–14}. Although alumina-supported sulfided Pt-Re bimetallic catalysts have been used industrially for decades in naphtha reforming^{15–21}, the un-sulfided version of this catalyst exhibits very interesting catalytic performance in liquid water.

In the early 2000's, Dumesic and co-workers reported that monometallic platinum group metals catalyze the aqueous phase reforming (APR) of biomass-derived molecules²². Soon thereafter, several monometallic and bimetallic catalysts based on transition group metals were developed to reform glycerol, a waste product of fatty acid transesterification to produce biodiesel^{23–25}. Promotion of carbon-supported Pt nanoparticles with a second oxophilic metal increased the rate of glycerol reforming to H₂, CO, CO₂, and light alkanes in liquid water by an order of magnitude compared to monometallic Pt^{1–3}.

Supported platinum group nanoparticles are also effective catalysts for the hydrogenolysis of glycerol. The hydrogenolysis of glycerol is often carried out at temperatures lower than that for APR to maximize the selectivity to propanediols^{26–29}. Daniel et al. reported that the addition of Re to Pt increased the rate of glycerol hydrogenolysis substantially and shifted the product selectivity from almost exclusively terminal hydrogenolysis, which produces 1,2-propanediol (1,2-PDO), toward internal hydrogenolysis, which formed 1,3-propanediol (1,3-PDO)⁴. At temperatures as low as 393 K, monometallic Pt, Rh, or Ir catalysts are nearly inactive for glycerol hydrogenolysis, but the addition of Re increases the rate of the reaction in liquid water and increases the selectivity of internal C-O bond hydrogenolysis^{7,30,31}. These types of bimetallic catalysts also demonstrate high activity and selectivity for the hydrogenolysis of other α,β -oxygen substituted substrates like 2-(hydroxymethyl)tetrahydropyran and tetrahydrofurfuryl alcohol^{7,32,33}.

In this chapter, the synthesis and characterization of the Pt-Re catalysts studied in this dissertation and the glycerol hydrogenolysis reaction used to test their catalytic performance will be discussed. All Pt-Re catalysts were synthesized by the successive incipient wetness impregnation of two different supports by an aqueous solution of a Pt precursor, followed by an aqueous solution of a Re precursor. Following incipient wetness impregnation, catalysts were treated with different gases at elevated temperatures to decompose the metal precursors and form the metal particles. A study was carried out to identify the treatment gas and temperature that yielded the best performance in glycerol hydrogenolysis. Further characterization of the Pt-Re catalysts using H₂ chemisorption to quantify exposed Pt sites, inductively coupled plasma atomic emission spectroscopy (ICP-AES) to measure the weight percent of Pt and Re, and transmission electron microscopy to determine the average particle size will be discussed.

3.2 Experimental Methods

3.2.1 Catalyst Preparation

All catalysts were prepared by incipient wetness impregnation of metal precursors followed by a thermal treatment. The Pt-Re bimetallic catalysts were synthesized by successive impregnation of the Pt precursor followed by the Re precursor. The platinum precursor used was Pt(NH₃)₄(NO₃)₂ (Sigma Aldrich) or H₂PtCl₆ (Sigma Aldrich), and the Re precursor used for all of the catalyst was NH₄ReO₄ (Sigma Aldrich). For a typical catalyst preparation, the Pt precursor was dissolved in a predetermined amount of distilled, deionized water to cause the silica gel support (Fuji Silysia G6) or the activated carbon support (Vulcan 72-XC) to reach incipient wetness. After the Pt solution was slowly added and thoroughly mixed with the support, the catalyst was dried overnight at 393 K in air. The Re precursor was then dissolved in water and the second impregnation was performed in the same manner. The resulting catalyst was then dried overnight in air at 393 K.

Before any measurements or reactions were performed, the bimetallic and monometallic Pt catalysts were heated to the desired temperature and reduced for 3 hours in 100 cm³ min⁻¹ of flowing H₂ (GTS Welco, 99.999%), He (GTS Welco, 99.999%), or air (GTS Welco, medical). For the catalysts that were treated in H₂, a passivation gas (GTS Welco, 1.03% O₂ balance N₂) was introduced to the catalyst for 30 min after the catalysts were stored in the catalysts were stored in the catalyst were stored

air at room temperature in a closed vial. The monometallic Re catalyst was calcined in flowing air at 773 K.

A "washing" procedure was also developed to remove spectator perrhenate that may be weakly-held on the silica support of 8 wt% Pt-Re/SiO₂. Briefly, 1.5 g of 8 wt% Pt-Re/SiO₂ was loaded into a downward flow stainless steel tube with a K-type thermocouple placed into the reactor bed. The reactor was purged with flowing N₂ (GTS Welco, 99.999%) at atmospheric pressure for 30 min followed by flowing H₂ for 30 min. Next, the catalyst was reduced in flowing H₂ at 473 K for 1 h at 1 MPa of pressure, which was maintained by a back pressure regulator. The catalyst was then cooled in H₂ to 393 K and distilled, deionized water, which was purged of air and saturated with 1 MPa of H₂, was introduced to the catalyst bed at a liquid flow rate of 2 cm³ min⁻¹ using an HPLC pump. After flowing for 30 min, so that the number of residence times of liquid water in the reactor was approximately 30, the water was purged from the system with H₂ and fully dried at 403 K in flowing H₂. The catalyst was subsequently cooled to room temperature and removed from the reactor. The resulting "washed" catalyst is referred to as 8 wt% Pt-Re/SiO₂-W.

3.2.2 Catalyst Characterization

The total number of hydrogen adsorption sites was determined by H_2 chemisorption using a Micromeritics ASAP 2020 automated adsorption analyzer. Samples were first heated at 4 K min⁻¹ and reduced at 473 K in flowing H_2 for 1.5 h. Next, the samples were evacuated for 2 h at 473 K and then another 2 h at 308 K. After the evacuation, analysis was performed at 308 K in the pressure range of 75 to 450 Torr. The total number of hydrogen adsorption sites was calculated by extrapolating the total amount of H_2 adsorbed in the saturated region to zero pressure to remove contributions from physisorbed hydrogen. Elemental analysis (using ICP–AES performed by Galbraith Laboratories, 2323 Sycamore Drive, Knoxville, TN 37921) was used to determine the Pt and Re weight loadings of the Pt-Re bimetallic catalysts. Transmission electron microscopy (TEM) images of the catalysts were acquired with an FEI Titan operated at 300 kV and equipped with a Gatan 794 Multi-scan Camera and an energy dispersive spectrometer for elemental X-ray analysis. Samples for microscopy were prepared by dipping TEM grids into a mixture of approximately 50 mg of catalyst and 7 cm³ of cyclohexane, which was sonicated for 15 min. To evaluate the particle size of the sample, the diameter of over 300 individual particles was measured for each sample.

Thermogravimetric analysis was performed using a TA Instruments SDT Q600. Briefly, approximately 6 mg of catalyst was loaded into an alumina crucible after taring the balance. The gas used to treat the catalyst, either H₂, He, or synthetic air (21% O_2 balance He), was then introduced at a flow rate of 100 cm³ min⁻¹ to stabilize the balance and purge out any residual atmosphere. Finally, the furnace was heated to the desired temperature at a ramp rate of 10 K min⁻¹.

3.2.3 Glycerol Hydrogenolysis

Glycerol hydrogenolysis reactions were performed in a 300 cm³ Parr autoclave equipped with a glass liner, PID-controlled heater, magnetically-driven stir bar, and a dip tube for periodic sampling. The reaction solution was prepared by diluting glycerol (Acros Organics, ACS Grade) with distilled, deionized water. For a typical reaction, catalyst was loaded into the autoclave and the solution was loaded into a separate reactant vessel that was wrapped with heating tape. The appropriate amount of catalyst was loaded into the empty reactor to give a ratio of moles of glycerol to total moles of Re (Gly/Re) equal to 150. After the contents were sealed in their respective containers, H_2 was used to purge the reactor and the reactant solution vessel for 20 min at atmospheric pressure. To re-reduce the catalyst after exposure to air, an in situ reduction was performed at 393 K and 1.4 MPa of H_2 for 1 hour. The reactant vessel was then heated to the reaction temperature of 393 K. When the reactant vessel reached the desired temperature, the solution was charged into the reactor and the reactor was pressurized to the desired pressure with H_2 . An initial sample of the reaction medium was taken through the dip tube while keeping the reactor sealed. The desired pressure of H_2 was maintained throughout the reaction by constantly feeding H₂. Samples were taken periodically throughout the course of the reaction and were analyzed using an Alliance high performance liquid chromatograph (Waters e2695) equipped with a refractive index detector (Waters 2414) and an Aminex ion exclusion column (Bio-Rad, HPX-87H) operating at 318 K with a 0.5 M H_2SO_4 mobile phase. Calibration curves were obtained using known concentrations of reactants and products.

The conversion was calculated as the total moles of products divided initial moles of glycerol and the selectivity for a specific product was the moles of that product divided by the total moles of product. The only products observed for glycerol hydrogenolysis at 393 K with H₂ in the headspace were 1,2-PDO, 1,3-PDO, 1-propanol (1-Prop), and 2propanol (2-Prop). All glycerol hydrogenolysis reactions performed in this work had a carbon balance between 90 and 105%. For simplicity, the ratio of C-O cleavages at secondary carbons versus primary carbons was calculated as the Sec:Prim ratio to compare selectivities for reactions performed with different catalysts. This number was calculated using the concentrations of the final products as shown below.

$$\frac{Sec}{Prim} = \frac{[1,3-PDO] + [1-Prop]}{[1,2-PDO] + 2*[2-Prop] + [1-Prop]}$$

3.3 Results and Discussion

3.3.1 Catalyst Characterization

The properties of the supported bimetallic catalysts, synthesized with a treatment in H_2 at 723 K, are summarized in Table 3.1. Vulcan carbon and Silica gel were used as supports to permit interrogation of the Pt-Re nanoparticles by NAP-XPS (Chapter 4) and infrared spectroscopy (Chapter 5), respectively.

Dihydrogen chemisorption was used to estimate the number of exposed Pt sites on the bimetallic catalysts. Previous studies revealed that the uptake of chemisorbed hydrogen on supported monometallic Re catalysts is below the detection limit.⁴ The results in Table 3.1 show the bimetallic catalysts chemisorbed more hydrogen compared the monometallic Pt catalysts indicating a greater fraction of the Pt was exposed. This is partly attributed to the fact that the Pt-Re catalysts had smaller particle sizes compared to the monometallic Pt catalysts, as revealed by TEM. This trend was especially evident on the Vulcan-supported catalysts. The bimetallic 8 wt% Pt-Re/C catalyst had a significantly higher H/Pt ratio than the 8 wt% Pt/C catalyst and the number average particle size measured by TEM was about half the size of the monometallic catalyst. Moreover, the monometallic Pt/C catalysts also had much broader particle size distributions that included some particles greater than 20 nm. In fact, the bimetallic catalysts had narrower particle size distributions compared to the corresponding monometallic catalysts, regardless of support. The particle size distributions for the catalysts in Table 3.1 are depicted in Figure 3.1. The consistently smaller particle sizes of the Pt-Re bimetallic catalysts indicates a stabilization of Pt against sintering at elevated temperatures by the presence of $Re^{2,34}$.

Catalyst	Support	Pt ^a (wt%)	Re ^a (wt%)	Re/Pt ^a	H uptake ^c (µmol/g)	H/Pt ^c	Average Diameter ^d (nm)	Surface Average Diameter ^e (nm)
8 wt% Pt-Re/SiO ₂	Silica Gel	7.0	6.8	1.0	155	0.38	2.4 ± 0.95	3.2
8 wt% Pt-Re/SiO ₂ -W	Silica Gel	6.3	5.3	0.89	135	0.33	2.6 ± 0.89	3.2
8 wt% Pt/SiO ₂	Silica Gel	8.0^{b}	-	-	118	0.30	4 ± 2.4	8.0
8 wt% Pt-Re/C	Vulcan Carbon	7.2	6.5	0.95	136	0.33	4 ± 3.2	9.6
8 wt% Pt/C	Vulcan Carbon	8.0^{b}	-	-	16	0.039	7 ± 7.3	27
4 wt% Pt-Re/C	Vulcan Carbon	3.7	3.6	1.0	85	0.41	1.7 ± 0.41	1.9
4 wt% Pt/C	Vulcan Carbon	4.0 ^b	-	-	56	0.27	2 ± 1.5	5.1

Table 3.1: Results from H_2 chemisorption and electron microscopy of Pt and Pt-Re catalysts.

aObtianed via ICP-OES, unless otherwise stated.

^bNominal weight loadings.

^cObtained via H_2 chemisorption at 308 K after the catalysts were reduced in situ at 473 K. ^dObtained via TEM.

^eObtained via TEM by $\Sigma d^3/\Sigma d^2$.

Table 3.1 also summarizes the properties of 8 wt% Pt-Re/SiO₂-W, which is catalyst that has been "washed" to remove weakly-held, water-soluble perrhenate that was not associated with the Pt on 8 wt% Pt-Re/SiO₂. Vicente et al. report that Re catalysts synthesized via incipient wetness impregnation of aqueous perrhenate results in well-dispersed, but weakly-held species on silica supports³⁵. Therefore, it is likely that some weakly-held perrhenate ions were present on the silica-based Pt-Re bimetallic catalysts used in this work. In addition, silica-supported perrhenate has been shown to expose Brønsted acid sites¹². The "washing" procedure is described in Section 3.2.1.



Figure 3.1: Particle size distributions obtained using TEM for a) 8 wt% Pt-Re/C b) 8 wt% Pt-Re/SiO₂ c) 8 wt% Pt/C and d) 8 wt% Pt/SiO₂.

3.3.2 Glycerol hydrogenolysis

The rates and selectivities of glycerol hydrogenolysis at 393 K in a 110 mM aqueous glycerol solution with 4 MPa of H₂ over 8 wt% Pt-Re/SiO₂, 8 wt% Pt-Re/SiO₂-W, and 8 wt% Pt-Re/C are presented in Table 3.2. Two measures of activity are presented in Table 3.2, one normalized to the mass of the catalyst, and the other normalized to the hydrogen uptake measured via H₂ chemisorption to give a turnover frequency (TOF). The TOF is one way to report a rate that properly accounts for differences in exposed metal attributed to differences in particle size. Unfortunately, the different affinity of Re and Pt for hydrogen means that the TOF expressed here is still based on an approximation of exposed active sites. Nevertheless, we observed that the Pt-Re nanoparticles supported on

silica had a higher activity per mass of catalyst as well as a higher TOF compared to the Vulcan-supported bimetallic catalyst. While the rate was higher on the silica-supported catalyst, the Sec:Prim ratio (a ratio of internal hydrogenolysis products to terminal hydrogenolysis products defined in Section 2.2.3) was lower on the silica-supported catalyst when compared to carbon-supported catalyst, indicating that the carbon-supported catalyst was more selective to internal hydrogenolysis reactions. In general, at 393 K in a 110 mM aqueous glycerol solution with 4 MPa of H₂, we observed the Sec:Prim ratio on silica-supported bimetallic catalysts to range between 0.5 and 0.6 whereas the ratio on the carbon-supported bimetallic catalysts was between 0.65 and 0.8. The Sec:Prim ratio was relatively independent of the glycerol conversion, up to 55%. A time profile of glycerol hydrogenolysis on 8 wt% Pt-Re/SiO₂ is presented in Figure 3.2.

As seen in Table 3.2, the rate of glycerol hydrogenolysis per mass of catalyst of the "washed" catalyst (8 wt% Pt-Re/SiO₂-W) was approximately 60% of the rate of the "unwashed" catalyst (8 wt% Pt-Re/SiO₂), while the Sec:Prim ratio was slightly higher on the "washed" catalyst. In Table 3.1, ICP-OES results show that the Re/Pt ratio decreased by approximately 11%, indicating that some Re was removed from the catalyst as a result of "washing". In addition, the hydrogen uptake measured via H₂ chemisorption decreased slightly. The particle size analysis, however, showed that the metal particle size did not change significantly during the washing procedure. In light of the reactivity results in Table 3.2, we conclude that the washing procedure did not significantly alter the nature of the active sites. The main goal of the washing procedure was to ensure that all soluble perrhenate was removed from the catalyst.

Catalyst	Time (min)	Conversion (%)	Rate (µmol g ⁻¹ min ⁻¹)	TOF ^a (s ⁻¹)	Sec:Prim
8 wt% Pt-Re/SiO ₂	60	8.3	98	0.0105	0.55
8 wt% Pt-Re/SiO ₂ -W	90	9.1	59	0.0073	0.64
8 wt% Pt-Re/C	240	6.5	17	0.0021	0.77

Table 3.2: Results from glycerol hydrogenolysis over 8 wt% Pt-Re/SiO₂, 8 wt% Pt-Re/SiO₂-W, and 8 wt% Pt-Re/C.

Reaction Conditions: 393 K, 4 MPa H₂, 90 cm³ 110 mM glycerol solution, Gly/Re=150 In situ pretreatment: 393 K, 1.4 MPa H₂ for 1 h

^aNormalized by H chemisorption uptake

The monometallic Pt/SiO₂ catalyst demonstrated a glycerol conversion of only 0.3% after 34 h of reaction at 393 K (utilizing three times the catalyst loadings used for results in Table 3.2), which corresponds to a TOF over monometallic Pt of 4.2 x 10^{-6} s⁻¹. Conversion of glycerol was not observed on 8 wt% Pt/C at 393 K because of its very low dispersion of Pt. Daniel et al. showed that at 473 K, a temperature at which monometallic Pt supported on Norit activated carbon had some measurable activity, the TOF of their Pt-Re/C catalyst was over an order of magnitude higher than Pt/C. That study also showed that their carbon-supported monometallic Re catalyst was inactive for glycerol hydrogenolysis at 473 K⁴. Clearly, the promotional effect of adding Re to supported Pt catalysts was observed, regardless of the support.



Figure 3.2: The glycerol conversion (\blacklozenge) and the Sec:Prim ratio (\blacksquare) throughout the course of glycerol hydrogenolysis at 393 K in a 110 mM aqueous glycerol solution on 8 wt% Pt-Re/SiO₂.

3.3.3 Synthesis of Pt-Re Catalysts for Glycerol Hydrogenolysis

Table 3.3: Glycerol hydrogenolysis results on Pt-Re bimetallic catalyst supported on Silica gel and Vulcan carbon synthesized with different Pt precursors.

Pt Precursor	Support	Conversion (%)	Rate (µmol g ⁻¹ min ⁻¹)	TOF ^a (s ⁻¹)	Sec:Prim	
Pt(NH ₃) ₄ (NO ₃) ₂	SiO ₂	6.9	35	0.0066	0.47	
H ₂ PtCl ₆	SiO_2	6.8	8.6	0.0039	0.39	
$Pt(NH_3)_4(NO_3)_2$	Vulcan Carbon	6.0	7.5	0.0015	0.80	
H_2PtCl_6	Vulcan Carbon	8.0	6.8	0.0013	0.69	
Reaction Conditions: 393 K, 4 MPa H ₂ , 90 cm ³ 110 mM glycerol solution,						

Gly/Re=150

In situ pretreatment: 393 K, 1.4 MPa H₂ for 1 h

^aNormalized by H₂ chemisorption uptake

Switching the Pt precursor from Pt(NH₃)₄(NO₃)₂ to H₂PtCl₆ to make 8 wt% Pt-

Re/SiO₂ decreased the TOF of hydrogenolysis by almost 50%, but the Sec:Prim ratio only

changed from 0.47 to 0.39 at 7% conversion. Interestingly, the change in Pt precursor only slightly decreased the rate of hydrogenolysis and the Sec:Prim ratio when Vulcan carbon was used as the support, as shown in Table 3.3.

The catalysts described in Table 3.1 were synthesized with $Pt(NH_3)_4(NO_3)_2$ and a thermal treatment in flowing H₂ at 723 K following work previously completed in our lab by Daniel et al⁴. In the current work, catalysts synthesized with thermal treatments in other gases and at other temperatures were compared for their performance in glycerol hydrogenolysis. The performance in glycerol hydrogenolysis and H₂ uptake of these catalysts treated in flowing H₂, He, or air are listed in Table 3.4. The pretreatment temperature for the He treated catalyst presented in Table 3.4 was chosen to appropriately compare the performance with the H₂ treated catalyst. The pretreatment temperature for the air treated catalyst was chosen based on work by Tomishige and co-authors who synthesize both Rh-Re and Ir-Re catalysts using a calcination or air thermal treatment step at 773 K. As is shown in Table 3.4, the H₂ treated catalyst revealed the highest activity for glycerol hydrogenolysis followed by He; the calcined catalyst in Entry 3 exhibited the lowest rate of the catalysts studied. While the TOF and global rate varied significantly with treatment conditions, the Sec:Prim remained relatively constant.

Figure 3.3 shows the total and derivative mass loss during the treatment in the three different gases for a fresh silica-supported catalyst loaded with 8 wt% Pt and 7.6 wt% Re that had not experienced any thermal treatment. The mass loss via thermogravimetric analysis (TGA) followed the decomposition of the $Pt(NH_3)_4(NO_3)_2$ and NH_4ReO_4 precursors as a function of temperature. The total mass loss (Figure 3.3a) under H_2

treatment at 540 K was 11%, which equals the weight percent of nitrogen and oxygen in the metal precursors loaded onto the catalyst. Conversely, the total mass loss in both He and air at 600 K was only 9% suggesting that oxygen might possibly still be present on the catalyst as PtO_x and ReO_x^{36} . The results in Figure 3.3 also show, that at a ramp rate of 10 K min⁻¹, the precursors decomposed until approximately 540 K, when H₂ is used as the treatment gas. When He or air was used, decomposition was completed by approximately 600 K. The catalysts were also treated at a ramp rate of 5 K min⁻¹, but changing the ramp rate did not alter the thermogravimetric response significantly. Decomposition in He and air exhibited the same total mass loss and approximately the same derivative mass loss profile, but the catalytic performance of the differently treated materials in glycerol hydrogenolysis was different, as shown in Table 3.4.

Table 3.4: The H_2 chemisorption uptake and glycerol hydrogenolysis results for the silica-supported 8 wt% Pt and 7.6 wt% Re catalyst prepared with different thermal treatments

Pretreatment Gas	Pretreatment Temperature	H Uptake (μmol g ⁻¹)	Conversion (%)	Rate (µmol g ⁻¹ min ⁻¹)	TOF ^a (s ⁻¹)	Sec:Prim
H_2	723 K	172	11.2	110	0.0107	0.56
He	723 K	132	5.3	55	0.0069	0.52
Air	773 K	136	2.4	21	0.0026	0.52
(1)Air (2)H ₂	(1)773 K (2)723 K	145	4.6	44	0.0051	0.43
H_2	523 K	198	6.7	73	0.0061	0.54
H_2	923 K	184	2.5	26	0.0024	0.61

Reaction Conditions: 393 K, 4 MPa H_2 , 90 cm³ 110 mM glycerol solution, Gly/Re=150 aNormalized by H chemisorption uptake

An experiment was also performed in which the catalyst was first treated in air, then after the catalyst was cooled to room temperature, the catalyst was subjected to thermal treatment in H₂. After the H₂ treatment, the rate of glycerol hydrogenolysis increased slightly, but the catalyst suffered from lower selectivity to secondary C-O bond hydrogenolysis. This result agrees with what was observed by Deng et al.³⁷. Treating Ir-Re nanoparticles supported on KIT-6 in air and then H₂ prior to reaction resulted in the lowest rate of 1,3-propanediol production of the catalysts studied³⁷.



Figure 3.3: Mass loss as a function of temperature for silica-supported 8 wt% Pt and 7.6 wt% Re catalysts in different gases a) shows the percent change in total mass loss and b) shows the derivative mass loss. The solid line is in H₂, the dashed line is in He, and the dotted line is in air.

Once it was confirmed that the thermal treatment in H₂ produced the best catalytic performance for 8 wt% Pt-Re/SiO₂, the temperature of the H_2 step was altered since the results depicted in Figure 3.3 indicate that the metal precursors are completely decomposed between 500 and 550 K. Entry 5 in Table 3.4 shows that the catalyst treated in flowing H_2 at 523 K actually had a lower rate of glycerol hydrogenolysis compared to the catalyst treated at 723 K. The next entry shows, that when the H_2 treatment temperature was increased to 923 K, the catalyst also had inferior performance to the catalyst treated at 723 K. Therefore, even though the metal precursors were completely decomposed by 540 K, a higher temperature is required to synthesize Pt-Re particles with higher activity. If the treatment temperature was too high, however, the performance also suffered. Between the treatment temperatures of 523 and 723 K, there might be further mixing and potential sintering of both Pt and Re to form bimetallic nanoparticles, creating more active sites that require close contact of Pt and Re. Treatments from 723 and 923 K, increased the Sec:Prim ratio to give the highest desired selectivity for this set of catalysts, but the rate was lower than the other catalysts treated in H_2 . It must also be noted that no discernable correlation existed between the rate per total metal and the number of H_2 uptake sites for the results presented in Table 3.4. This lack of correlation likely indicates that it is not sufficient to have only H uptake sites (most likely on Pt metal) to obtain high rates of glycerol hydrogenolysis; evidently specific interactions between Pt and Re are required

Rønning et al. observed that when N_2 was used as to pretreat alumina-supported Pt-Re nanoparticles the Pt-Re coordination number from extended X-ray absorption fine structure (EXAFS) was close to zero³⁶. Treatment of the alumina supported catalyst in air however, enhanced the interaction between Pt and Re. They concluded that thermal treatment in an inert gas may prevent adequate migration of Re on the surface to form the desired Pt-Re nanoparticles, whereas oxygen will bond strongly with Re and weaken the Re-support interactions, thus increasing the mobility of the Re. Rhenium strongly interacts with alumina, but has a much weaker interaction with silica^{35,36}. Based on the results in Table 3.4, the treatment in He better facilitates the formation of Pt-Re nanoparticles with high activity for glycerol hydrogenolysis compared to treatment in air. Rønning et al. also observed that a treatment in air at 723 K yielded the highest H₂ uptake indicating calcination induced the highest dispersion of Pt for the Pt-Re catalysts studied, but reduction of Pt-Re/Al₂O₃ was not investigated in that work³⁶.

Ma et al. compared the performance of silica-supported Ru-Re nanoparticles that were reduced or calcined and found that reduction of the catalyst at 723 K resulted in the most selective catalyst to 1,3-PDO for glycerol hydrogenolysis³⁸. Conversely, calcination at 623 K produced the most active catalyst³⁸. Interestingly, Deng et al. observed that reduction of Ir-Re nanoparticles supported on KIT-6, an ordered mesoporous silica, yielded the most active and selective catalysts for glycerol hydrogenolysis to 1,3-PDO³⁷. In addition, reduction of Ir-Re/KIT-6 appeared to increase the resistance of the nanoparticles to sintering under reaction conditions compared to calcination. Particles larger than 10 nm where observed on the calcined catalyst after reaction indicating that particle agglomeration occurred, whereas the reduced catalyst did not appear to sinter during reaction³⁷. Tomishige and co-authors have studied the silica-supported Rh-Re and Ir-Re bimetallic systems extensively for the hydrogenolysis of glycerol and the ring opening of

cyclic ethers^{5,39,40}. In each of their works, catalyst were synthesized by a calcination step at 723 K and the conversion decreased only minimally when the catalyst was recycled and reused in second reaction indicating the catalyst was very stable. In summary, the optimal pretreatment for bimetallic Re catalyst depends on the late transition metal as well as the support used. It is important to note, however, that regardless of the catalyst pretreatment procedure, it is crucial to perform an in situ reduction of the Re bimetallic catalyst in H₂ before exposing the catalyst to the reaction environment. Daniel et al. observed that without an in situ H₂ treatment at 493 K, complete leaching of Re from carbon-supported Pt-Re was observed when the catalyst was introduced to liquid water⁴.

3.3.4 Glycerol hydrogenolysis using heterogeneous Pt and homogeneous acid

An experiment was performed to test whether or not it was sufficient to have the acid in solution together with supported Pt particles to produce 1,3-PDO during glycerol hydrogenolysis. An amount of HCl that was equivalent to the moles of Re on the 8 wt% Pt-Re/SiO₂ was added to the reaction medium with the monometallic 8 wt% Pt/SiO₂ catalyst. The reaction with HCl and 8 wt% Pt/SiO₂ had a TOF of only 5.5 x 10^{-5} s⁻¹ at very low conversion compared to a TOF of 0.0105 s⁻¹ observed on the bimetallic catalyst. Since the TOF on 8 wt% Pt/SiO₂ in the absence of HCl was 4.2 x 10^{-6} s⁻¹, the addition of HCl increased the rate by an order of magnitude, but it was still several orders of magnitude slower than 8 wt% Pt-Re/SiO₂.

Another reaction was conducted in which water soluble HReO₄ was added to the reaction medium together with 8 wt% Pt/SiO₂. In this experiment, the molar ratio of Re and Pt was also chosen to be 1:1. The TOF (based on exposed Pt) for the reaction with the

HReO₄ and 8 wt% Pt/SiO₂ was $1.6 \times 10^{-4} \text{ s}^{-1}$, which was nearly 300% higher than the TOF for 8 wt% Pt/SiO₂ with HCl. The increase in rate with the addition of Re suggests that perrhenate in solution may reduce onto the Pt nanoparticles during the course of the reaction and form the active sites that are present on the Pt-Re bimetallic catalyst. It also must be noted that the experiments with HCl and HReO₄ added to the reaction with 8 wt% Pt/SiO₂ demonstrated Sec:Prim ratios of 1.0 and 0.9, respectively, indicating internal C-O bond activation is more favored in acidic solutions. Moreover, both Pt and acid are required for high activity since conversion of glycerol was not observed in the presence of only acid. The results from experiments with the homogenous acids and supported Pt suggest that intimate contact of the Brønsted acid site and a Pt metal site is required to produce 1,3-PDO at a high rate from glycerol.

3.4 Conclusions

Bimetallic catalyst containing Pt-Re bimetallic catalysts synthesized using two different supports were characterized and tested for their performance in glycerol hydrogenolysis. The silica-supported catalyst was more active for glycerol hydrogenolysis and the carbon-supported catalyst was slightly more selective for activating secondary alcohols. While the support did play a secondary role in the catalytic performance of the nanoparticles, the mechanism of glycerol hydrogenolysis did not appear to change over these two supports. Upon "washing" the 8 wt% Pt-Re/SiO₂ catalyst in flowing liquid water to remove soluble permeate species weakly held on the silica support, the results for glycerol hydrogenolysis did not appear to change significantly. A thermal treatment in flowing H₂ at 723 K during the synthesis produced the catalyst with the highest rate for

glycerol hydrogenolysis. Thermal treatments in He, air, and at temperatures different than 723 K in H₂ yielded inferior catalysts. No trend was observed between the amount of chemisorbed H₂ and the rate of glycerol hydrogenolysis with different thermal treatments indicating it is not sufficient to have only H₂ uptake sites, associated with Pt metal on the catalytic surface, to obtain high rates of glycerol hydrogenolysis. Experiments performed with a monometallic Pt catalyst and homogenous acid suggest that close contact between Pt and Re on the surface of the catalyst is required to obtain high rates of glycerol hydrogenolysis with high selectivity to 1,3-PDO.

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Chapter 4: X-ray Photoelectron Spectroscopy of Pt-Re

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4.1 Introduction

The oxidation state of Re in the working state of the bimetallic catalysts is still unknown even though the oxidation state of Re in Pt-Re bimetallic catalysts has been under investigation for several decades¹. One of the reasons for the ambiguity regarding the oxidation state of Re is its dependence on the conditions to which the Re is subjected. The reduction of Re⁷⁺, or perrhenate (the most stable oxidation state), usually does not begin until approximately 573 K², but can occur as low as 373 K in the presence of Pt because of hydrogen spillover³. Since Re is oxophilic, the partially-reduced Re in the Pt-Re bimetallic catalyst is oxidized to Re⁷⁺ upon exposure to air. Therefore, the oxidation state of Re depends on the pretreatment of the catalyst and the conditions under which the catalyst is probed⁴.

Recently, in situ X-ray absorption spectroscopy (XAS) has been used to study Pt-Re particles supported on Norit carbon³ as well as Rh-Re⁵ and Ir-Re⁶ particles supported on silica. The average oxidation state of Re in those works was determined to be approximately 2+ after reduction in flowing H₂ at temperatures between 373 and 473 K. Another study by Chia et al. concluded that Re in Rh-Re nanoparticles supported on Vulcan

carbon was metallic⁷. Interestingly, that work showed that the oxidation state of Re was the same in gaseous H_2 as well as under reaction conditions with H_2 -saturated water.

In this chapter, X-ray photoelectron spectroscopy (XPS) was used to study the oxidation state of Re in Pt-Re bimetallic catalysts supported on both Vulcan carbon and silica. The advantages of using XPS are that the various oxidation states can be discerned instead of an overall bulk average (obtained via XAS), and the technique is more sensitive to the elemental composition at the surface, which is most applicable to catalysis. In addition to using conventional XPS equipped with an Al K α radiation source, experiments were performed using a near ambient pressure X-ray photoelectron spectrometer (NAP-XPS), which allowed for measurements to take place in the presence of H₂ and water vapor at 393 and 473 K.

4.2 Experimental Methods

Both conventional X-ray photoelectron spectroscopy (XPS) and near-ambientpressure X-ray photoelectron spectroscopy (NAP-XPS) experiments were performed. Conventional XPS using a focused monochromatic Al K α X-ray radiation source (1486.6 eV) and a Thermo Scientific ESCALAB 250 spectrometer was carried out using at the Nanomaterials Core Characterization Facility of the Virginia Commonwealth University. A hemispherical analyzer with a 6-element multichannel detector was used. The incident X-ray beam was 45° off normal to the sample while the X-ray photoelectron detector was normal to the sample. A large area magnetic lens with a 500 µm spot size in constant analyzer energy mode was utilized with a pass energy of 20 eV for region scans. Charge compensation was employed during data collection with an internal electron flood gun (2 eV) and a low energy external Ar ion flood gun. Thirty region scans were taken with a step size of 0.1 eV for Pt and Re spectra.

Conventional XPS samples were prepared by pressing the powder catalyst onto a strip of Pb foil (ESPI Metals, 99.99%) that was secured onto a copper metal plate using an ultra-high vacuum carbon paste (Ted Pella, PELCO); the copper plate was then attached to a sample holder. No Pb features were observed in the XPS survey scans ensuring that the powder was thick enough that interactions between the Pb and the catalyst did not interfere with the measurements. To reduce the catalyst prior to conventional XPS analysis, the sample holder was placed in a reduction cell attached to the preparation chamber. After flushing the reduction cell three times with H_2 and pressurizing it to 0.2 MPa, the cell was heated to the desired temperature in H_2 for 1 h. After reduction, the cell was allowed to cool to room temperature and the sample was transferred from the reduction cell to the preparation chamber, which was at a pressure of approximately 10⁻⁶ mbar. The sample was then transferred from the preparation chamber over the course of about 5 min. The analysis chamber was maintained at a pressure of 10⁻⁹ mbar and was constantly purged with the Ar ion flood gun. To infer the amount of oxidation that occurred in the preparation chamber during the 5 min transfer an experiment was performed during which the sample remained in the preparation chamber for 90 min after reduction.

The NAP-XPS experiments were performed at the Innovative Station for In Situ Spectroscopy (ISISS) beamline at the Helmholz-Zentrum Berlin/BESSY II synchrotron facility using a Phoibos 150 hemispherical energy analyzer. The advantages of this instrument were that the photon energy can be tuned between 80 and 2000 eV and measurements can be made in pressures up to 0.3 mbar. More work using this system as well as a complete description of the equipment can be found elsewhere^{2,8-10}. The pressure in the analysis chamber is maintained by simultaneous operation of mass flow controllers, to control the flow of gases, and a feedback-regulated valve between the chamber and a turbo molecular pump, to regulate the rate of pumping. The spectrometer utilizes a hemispherical analyzer that is operated in ultrahigh vacuum. The pressure difference between the reaction cell and the analyzer is maintained using three differentially pumped stages. Each stage consists of an electrostatic lens for gathering a wide-angle spread of photoelectrons and focusing the electrons onto the analyzer entrance slit. Since this arrangement was not amenable to utilizing charge compensation devices, measurements were only performed using the 8 wt% Pt-Re/C catalyst. The silica-supported catalyst charged significantly and reliable measurements could not be made. For each condition studied, measurements were recorded at three different kinetic energies (150, 500, and 1000 eV) by adjusting the photon energy – so that the difference between the photon energy and the kinetic energy equaled the appropriate binding energy. Spectra of Pt and Re were measured by averaging thirty scans using a pass energy of 10 eV and a step size of 0.05 eV. The total Gaussian resolution for the combination of photon source and spectrometer was 0.2 and 0.5 eV for the measurements with kinetic energies of 150 and 1000 eV, respectively. The core level binding energies for the NAP-XPS results were calibrated by first measuring the kinetic energy difference between the C 1s first and second order peaks to find the true kinetic energy of the C 1s first order peak, which was approximately 284.2 eV. Next the same photon energy used to obtain the Pt and Re spectra was used to measure

C 1s binding energy at every condition studied. The Pt and Re peaks were then calibrated to those C 1s spectra, which were assigned to 284.2 eV. The accuracy of the binding energy calibration was estimated to be approximately 0.1 eV.

The 8 wt% Pt-Re/C sample for NAP-XPS was prepared by first pressing the catalyst into a pellet. The pellet was then secured between one solid metal plate and one plate with a 3 mm diameter hole. The catalyst was heated via an infrared laser that was focused at the back of the solid metal plate using a fiber-optic cable and infrared optical elements. The temperature was measured with a K-type thermoelement that was secured between the metal plates in close proximity to the catalyst. In a typical experiment, the sample was loaded into the analysis chamber at room temperature and pressure of about 10⁻⁷ mbar. Next, H₂ was introduced at 5 cm³ min⁻¹ while the pressure was maintained at 0.3 mbar. The temperature was then increased to the desired temperature at a ramp rate of 10 K min⁻¹. The sample remained at the desired temperature for at least 20 min before any measurements were performed. Scans were recorded during the course of the experiment to ensure the catalyst was not changing and that it reached a stable state. After the measurement in the presence of H₂, H₂O and H₂ were introduced together at 5 cm³ min⁻¹ each and the system was allowed to equilibrate for 20 min, before additional measurements were taken. Finally, the H₂ flow was halted so that only H₂O was introduced to the chamber. The H₂O was cryogenically-distilled with liquid nitrogen to remove any air or other impurities.

For the silica-supported catalysts, the binding energies of all species were referenced to the Si 2p feature at 103.7 eV. The conventional XP spectra for the Vulcan-

supported catalyst were referenced to the C 1s feature at 284.2 eV. Spectra obtained from both conventional XPS and NAP-XAS were deconvoluted with a curve fitting routine in CasaXPS while using several constraints. For platinum and rhenium, the 7/2 - 5/2spin-orbit coupling was set to 3.35 and 2.43 eV, respectively, and the 5/2 peak area was assigned to be 75% of the 7/2 peak area for both elements. The binding energies, FWHM, and lineshapes of the observed 7/2 Pt and Re species are shown in Table 4.1. The lineshapes of the 7/2 peaks were the same as the 5/2 peaks. Tougaard backgrounds were used to fit the Pt peaks and Shirley backgrounds were used to fit the Re peaks. To calculate the Re/Pt molar ratio the area under the photoemission response curves from Pt and Re, minus the background, were by corrected by the atomic subshell photoionization cross sections¹¹ and the photon flux in NAP-XPS.

The curve fitting parameters listed in Table 4.1 were used in the CasaXPS software to deconvolute XP spectra. The peak positions and widths (FWHM) were allowed to float between the ranges listed in the table. The peak lineshapes follow syntax used by the CasaXPS software to invoke certain lineshape functions chosen based on the metal or metal oxide being fit. The lineshapes called DS(x,y)GL(z) are actually composite lineshapes consisting of Doniach-Sunjic and Gaussian-Lorentzian functions. The lineshapes listed in Table 4.1 were used to deconvolute Pt and Re spectra obtained using conventional XPS and NAP-XPS at all energies. The only exception was the Pt 4f spectra at 150 eV which used the lineshape LA(1.5,2,10). Lineshapes for Pt and Re were modified from work conducted by Biesinger¹² and Greiner et al.², respectively.
Species	Pt (0)	Re(0)	Re(II)	Re(IV)	Re(VI)	Re(VII)	Re(46.6)
Position	70.9 - 71.9	40.0 - 41.0	41.1 - 41.5	42.1 - 42.7	42.8 - 43.5	45.0 - 46.0	47.2 - 47.8
FWHM	1.4 - 2.0	0.6 - 1.0	0.6 - 1.0	1.3 - 1.8	1.3 - 1.8	1.6 - 2.1	1.6 - 2.1
Lineshape	LA(1.2,85,70)	DS(0.1,200) GL(80)	DS(0.07,200) GL(80)	DS(0,300) GL(60)	DS(0,300) GL(60)	GL(65)	GL(10)

Table 4.1: XPS curve fitting parameters used in CasaXPS (Version 2.3.16).

4.3 Results

4.3.1 Conventional X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was used to ascertain the oxidation states of Pt and Re after the supported nanoparticles were reduced at the moderate temperatures used in the reaction conditions of this study. Before measurements of the catalysts were performed, conventional XPS of Re standards was conducted using Al K α radiation, the spectra of which are shown in Figure 4.1. All of the Re standards were characterized "as is" from the manufacturer with no further pretreatment. Multiple Re oxidation states were observed in all of the spectra because the surfaces of the samples readily oxidize in air. In fact, the most thermodynamically-stable Re oxide is $Re_2O_7^2$. Since Al K α radiation at 1486.6 eV was used to measure photoemission spectra of the Re standards, the inelastic mean free path of the electrons was approximately 1.6 nm, which means photoelectrons from the bulk material will also contribute to the overall signals¹³. The majority of the photoemission response in the conventional XP spectra (Figure 4.1) of Re metal (Re^{0}), ReO_2 (Re^{4+}), and ReO_3 (Re^{6+}) standards can be ascribed to the bulk material. The Re $4f_{7/2}$ binding energies for Re⁰, Re⁴⁺ and Re⁶⁺ were 40.5, 42.6, and 43.5 eV, respectively, and compare well with reported values^{1,2,14}. To estimate the binding energy of Re⁺⁷, NH₄ReO₄ was used as the standard since this particular Re salt was used to prepare the catalysts. Two Re species were observed in this sample, which had $4f_{7/2}$ peaks at 45.7 and 47.4 eV. The 47.4 eV $4f_{7/2}$ peak has been observed by others for NH₄ReO₄, while a 45.7 eV $4f_{7/2}$ peak is most likely attributed to Re₂O₇^{2,15,16}. In addition to features associated with the stable bulk oxides of Re, a $4f_{7/2}$ peak with a binding energy of 41.5 eV was also observed in the spectrum of Re metal (Figure 4.1), which has been ascribed to ReO (Re⁺²)^{2,14}. It should be noted that ReO is not stable as a bulk material, but it has been observed at the interface of higher oxidation state oxides and Re metal^{2,14,17}.

Once the binding energies for all of the standard Re oxide peaks were determined, the photoemission spectra of Pt-Re catalysts were then analyzed using the CasaXPS fitting software with constraints that are described in Section 4.2. The Pt 4f and Re 4f conventional XP spectra of 8 wt% Pt-Re/C and 8 wt% Pt-Re/SiO₂, exposed to air without in situ reduction, are shown in Figure 4.2. Even without in situ reduction, the Pt 4f spectra in Figure 4.2 reveal binding energies for the $4f_{7/2}$ and $4f_{5/2}$ peaks of approximately 71.1 and 74.4 eV, respectively, which correspond to metallic Pt. In fact, the spectra for all of the catalysts studied in this work revealed that Pt was always metallic. The results for the Re binding energies, however, depended strongly on the pretreatment conditions.



Figure 4.1: Conventional XPS of Re standards with no pretreatment. The grey dots are the data and the dotted black lines are the results from peak fitting.



Figure 4.2: Spectra from conventional XPS of 8 wt% Pt-Re/C and 8 wt% Pt-Re/SiO₂ without in situ reduction. The grey dots are the data and the dotted black lines are the results from peak fitting.

Figure 4.2 also shows the 4f photoemission spectra of the Re component of the catalysts with results from curve fitting tabulated in Table 4.2. In contrast to Pt, the Re component of the bimetallic catalysts oxidizes readily when exposed to air³. In addition, the degree of Re oxidation by air exposure was different on the two catalysts studied. The peak fitting results show that most of the Re in 8 wt% Pt-Re/C had an oxidation state of Re⁺⁷, which is consistent with the previously reported XANES of Pt-Re bimetallic catalysts supported on Norit Activated Carbon³. The conventional XPS results from this work also revealed that a very small portion of the Re was present as Re metal (Re⁰) and ReO₂ (Re⁺⁴). For the silica-supported catalyst, the Re component of the catalyst was more evenly

distributed among the various oxidations states corresponding to Re⁰, Re²⁺, Re⁴⁺, and Re⁷⁺. In addition, two peaks with binding energies of 47.4 and 49.8 eV were observed, which are close to the binding energies of peaks observed in the spectra of NH₄ReO₄ (Figure 4.1). Because the NH₄ReO₄ precursor should have decomposed during the 723 K reduction treatment used in the catalyst synthesis procedure, we ascribe these peaks to Re⁷⁺-like species^{1,16}, which are well dispersed, but weakly-held on the silica support¹⁸. Peaks with binding energies of 47.4 and 49.8 eV were not observed in the 8 wt% Pt-Re/C catalyst, even though the same reduction conditions were used for the 8 wt% Pt-Re/SiO₂ catalyst during synthesis. Evidently, the weakly-held perrhenate species was not as stable on the carbon support after the reduction treatment as it was on silica.

Table 4.2: Composition and distribution of Re oxidation states in 8 wt% Pt-Re/C and 8 wt% Pt-Re/SiO₂ catalysts evaluated by conventional XPS*.

0 wt/0 1 t-KC/C							
	Distribution of Re Oxidation States						
Reduction Temperature	Re(0)	Re(II)	Re(IV)	Re(VII)	Re/Pt		
No Reduction	7%	0%	11%	81%	1.80		
393 K	39%	13%	45%	3%	1.78		
473 K	59%	11%	31%	0%	2.21		
8 wt% Pt-Re/SiO ₂							
	Distrib	ution of F	Re Oxidation	on States			
Reduction Temperature	Re(0)	Re(II)	Re(IV)	Re(VII)	Re/Pt		
No Reduction	0%	13%	9%	77% ^a	3.63		
393 K	30%	34%	36%	0%	0.67		

8 wt% Pt-Re/C

473 K

^aContains the contribution from the Re $4f_{7/2}$ and $4f_{5/2}$ peaks with binding energies of 47.4 and 49.8 eV, respectively.

44%

6%

0%

0.60

51%

*Results were determined from curve fitting of the spectra acquired at room temperature. Some of the catalyst were reduced in situ in H_2 and then evacuated for 5 min prior to analysis.

The carbon-supported and silica-supported bimetallic catalysts were also studied after reduction in H₂ at 393 and 473 K in a cell attached to the conventional XPS system. Great care was taken to ensure that significant oxidation of the samples did not occur while they were being transferred from the reduction cell to the analysis chamber. To test the level of oxidation that might occur during the transfer, an experiment was performed during which the samples were left in the preparation chamber at 10^{-6} mbar for 90 min after reduction. These samples were compared to those that were transferred as quickly as possible through the preparation chamber, which was approximately 5 min. The percent contribution of each Re oxidation state from the curve fitting results of the Re 4f XP spectra for these experiments is summarized in Table 4.3. Even though the pressure in the preparation chamber was maintained at 10⁻⁶ mbar, some oxidation of the rhenium was observed after 90 min. This result shows that the rate of Re oxidation is extremely fast and great care must be taken to keep the Re reduced during reaction and characterization experiments. To determine the significance of the oxidation that occurred after 5 min, the percent contributions of the Re oxidation states at the 5 and 90 min time points were extrapolated to time zero, assuming a linear fit, which are also shown in Table 4.3 in italicized text. This extrapolation suggests that the oxidation occurring after 5 min in the preparation chamber was minimal and that the state of the catalysts after 5 min in the chamber closely resembles the state of the catalyst under reduced conditions.

Table 4.3: The distribution of Re oxidation states from the curve fitting analysis of 8 wt% Pt-Re/C and 8 wt% Pt-Re/SiO₂ after they were reduced in H₂ at 393 and 473 K. The time denotes how long the samples remained in the preparation chamber. The distributions at time=0 was extrapolated from a linear fit of the other two time points.

393 K

473 K

8 wt% PtRe/C

	Distribu	tion of R	le Oxidati	on States		Distribu	ition of R	e Oxidati	on States
Time	Re(0)	Re(II)	Re(IV)	Re(VII)	Time	Re(0)	Re(II)	Re(IV)	Re(VII)
0 min	39%	14%	44%	3%	0 min	60%	11%	31%	0%
5 min	39%	13%	45%	3%	5 min	59%	11%	31%	0%
90 min	40%	3%	56%	2%	90 min	48%	18%	34%	0%

8 wt% PtRe/SiO₂

	Distribu	tion of R	le Oxidati	on States			Distrib	oution of	Re Oxida	tion States
Time	Re(0)	Re(II)	Re(IV)	Re(VII)		Time	Re(0)	Re(II)	Re(IV)	Re(VII)
0 min	31%	34%	35%	0%		0 min	52%	46%	4%	0%
5 min	30%	34%	36%	0%		5 min	51%	44%	6%	0%
90 min	11%	30%	54%	6%	-	90 min	43%	11%	47%	0%

Conventional XPS results from the curve fitting of spectra for the catalysts reduced at 393 and 473 K in H₂ are also summarized in Figure 4.3 and Table 4.2. As mentioned previously, the Pt 4f spectra revealed that Pt was always in the metallic state on the samples, regardless of how the catalysts were pretreated prior to XPS. In contrast, a large portion of the Re remained in an oxidized state even after reduction in H₂ at 393 and 473 K. Furthermore, the distribution of Re oxidation states was influenced by reduction over this narrow temperature range. After a 1 h reduction at 393 K, Re⁰, Re²⁺, and Re⁴⁺ were observed on both carbon-supported and silica-supported catalysts while there was also a small percentage of Re⁺⁷ that was observed on the carbon-supported sample. The silicasupported catalyst appeared to be slightly more oxidized than the carbon supported catalyst since the ratio of Re²⁺/Re⁰ in the silica-supported catalyst was higher. The same general behavior was observed after the catalysts were reduced at 473 K – the silica-supported catalyst appeared to be slightly more oxidized than the carbon-supported catalyst. As expected, the distribution of Re oxidation states was shifted towards Re metal when the catalysts were reduced at 473 K compared to 393 K, but there was still a significant amount of Re in the +2 and +4 oxidation states on both catalysts under all of the conditions studied.



Figure 4.3: Re 4f spectra from conventional XPS of 8 wt% Pt-Re/C and 8 wt% Pt-Re/SiO₂ reduced at 393 and 473 K after only 5 min in the preparation chamber. The grey dots are the data and the dotted black lines are the results from peak fitting.

The Re/Pt ratio of the catalysts as evaluated by XPS was also affected by the support and reduction temperature. In the right most column of Table 4.2, the areas under

the photoemission response curves from Pt and Re were used to calculate the atomic ratio of Re/Pt associated with the bimetallic nanoparticles. The Re/Pt ratio for the carbonsupported catalyst did not appear to change as the catalyst was reduced at higher temperatures and the surface appeared to be slightly enriched in Re. The silica-supported catalyst, however, showed different behavior. As the reduction temperature was increased, the Re/Pt ratio indicates that the surface became enriched in Pt, while Re segregated to the core of the catalytic particles.

4.3.2 Near ambient pressure X-ray photoelectron spectroscopy

Additional characterization of the Re in 8 wt% Pt-Re/C exposed to various environments was obtained using a synchrotron-based near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) system. The two major advantages of this system were 1) the ability to tune the photon energy of the X-ray source, which allowed a range of sample depths to be probed and 2) the ability to perform measurements in the presence of reactant gases up to pressures of 0.3 mbar. Unfortunately, the silica-supported catalyst experienced significant charging effects during irradiation and reliable spectra could not be acquired because this system was not amenable to utilizing charge compensation devices.

The NAP-XPS measurements were performed on 8 wt% Pt-Re/C at three different kinetic energies under several different environmental conditions. The kinetic energy was changed by tuning the incident photon energy for each element of interest so that the photon energy minus the binding energy of the element equaled the desired kinetic energy of the photoelectrons. By recording measurements at kinetic energies of 150, 500, and 1000 eV,

the oxidation states of Pt and Re at different distances from the surface of the nanoparticles could be investigated. Table 4.4 shows the inelastic mean free path of the electrons from both Pt and Re at the three kinetic energies studied using the synchrotron-based technique as well as the inelastic mean free path of the conventional XPS experiments using Al K α radiation. Since the photon energy could not be tuned in the conventional XPS experiments, the kinetic energy of photoelectrons differed for Pt and Re by 30 eV, which is the difference in binding energy for the two elements.

Table 4.4: Inelastic mean free path for Pt and Re at the different kinetic energies used in conventional XPS and NAP-XPS measurements of this study. The inelastic mean free paths were obtained by software provided in citation 13.

	Inelastic Mean Free Path (nm)			
Kinetic Energy	Pt	Re		
150 eV	0.48	0.55		
500 eV	0.81	0.89		
1000 eV	1.25	1.40		
≈1400 eV*	1.82	1.60		

*The kinetic energy for Pt and Re was approximately 1416 and 1446 eV, respectively, since an untunable Al Kα radiation source was used.

Figure 4.4 shows the NAP-XPS of 8 wt% Pt-Re/C at three different kinetic energies at 393 and 473 K in 0.3 mbar of H₂. At both of these temperatures, the curve-fitting results show that as the kinetic energy of the photoelectrons increased, which corresponded to an increase in the probing depth, the oxidation state of the Re shifted towards Re metal. This result indicates that under reducing conditions at the temperatures studied, the Re closest to the surface of the nanoparticles was present in a range of oxidation states, and Re in the core of the nanoparticle had a lower oxidation state that was most likely metallic.



Figure 4.4: Re 4f NAP-XPS of 8 wt% Pt-Re/C, in 0.3 mbar of H_2 at 393 and 473 K, recorded at three different photoelectron kinetic energies. The grey dots are the data and the dotted black lines are the results from peak fitting.

The NAP-XPS results of the Pt component of the catalyst, presented in Figure 4.5, revealed that the Pt was also in the metallic state. Since only one set of $4f_{7/2}$ and $4f_{5/2}$ peaks was observed in the spectra, we conclude that Pt resides primarily in a single state in the bimetallic samples. The binding energy of the Pt $4f_{7/2}$ peak was approximately 71.1 eV for the measurements obtained with kinetic energies of 500 and 1000 eV, which has been

ascribed to metallic Pt¹⁹. The measurements obtained at a kinetic energy of 150 eV, however, revealed a shift in the binding energy of Pt of approximately 0.6 eV to around 71.7 eV. The Pt $4f_{7/2}$ binding energies for the NAP-XPS measurements are tabulated in Table 4.5. Duke et al. also observed a binding energy shift of approximately 0.55 eV in the Pt $4f_{7/2}$ peak upon the physical addition of Re to a Pt(111) single crystal using NAP-XPS at a photon energy of 545 eV^{14} . Interestingly, when the Re was removed via oxidation at 500 K, the Pt $4f_{7/2}$ binding energy returned to that associated with the clean crystal at 71.0 eV. In addition, the Pt L_{III} XANES of alumina-supported²⁰ and Norit carbon-supported³ Pt-Re nanoparticles were shifted to slightly higher energies than supported monometallic Pt nanoparticles. The fact that the white line intensity of the monometallic Pt was the same as that in the Pt-Re bimetallic sample indicates the Pt remained fully reduced in the presence of Re^3 . We ascribe the observed shift in the Pt $4f_{7/2}$ binding energy in the current work to an electronic interaction with Re on the surface of the nanoparticles. As mentioned above, the shift in binding energy was only evident at a kinetic energy of 150 eV, which suggests the affected Pt is mainly at the surface of the nanoparticles.



Figure 4.5: Pt 4f NAP-XPS of 8 wt% Pt-Re/C, in 0.3 mbar of H_2 at 393 and 473 K, recorded at three different photoelectron kinetic energies. The grey dots are the data and the dotted black lines are the results from peak fitting.

The quantitative results of the curve fitting of the NAP-XPS experiments in 0.3 mbar of H₂ and the conventional XPS measurements, after 8 wt% Pt-Re/C was treated in a separate reduction cell, are shown in Table 4.6. Trends in the distribution of Re oxidation states in Table 4.6 show good agreement between the two different XPS techniques. Conventional XPS and NAP-XPS also show that the distribution of Re oxidation states shifts towards Re metal as the reduction temperature increased from 393 to 473 K, as

indicated by the weighted average binding energy of the Re photoelectron response, which is tabulated in the table. Table 4.6 also presents conventional XPS and NAP-XPS results of the catalyst measured at room temperature in UHV. Again, these two techniques show general agreement in the distribution of Re oxidation states. Both techniques confirm that the Re on the surface of the catalyst was highly oxidized after it was exposed to air prior to any in situ reduction.

from the NAP-XPS results at different conditions.

Table 4.5: The Pt $4f_{7/2}$ binding energies (in eV) of the 8 wt% Pt-Re/C catalyst

Kinetic Energy H_2 $H_2 + H_2O$ H_2O H_2 $H_2 + H_2O$ 150 eV71.571.771.771.871.8		333 K
150 eV 71.5 71.7 71.7 71.8 71.8	H_2O	O_2
	71.8	71.7
500 eV 71.0 71.1 71.1 71.3 71.3	71.3	71.2
1000 eV 70.8 71.0 71.0 71.1 71.2	71.2	71.2

Since glycerol hydrogenolysis takes place in liquid water saturated with H_2 , the influence of water on the distribution of Re oxidation states and the Re/Pt ratio was studied using NAP-XPS. The curve fitting results of spectra taken at 150 eV, which are the most surface sensitive measurements, are tabulated in Table 4.7 and the photoemission spectra are shown in Figure 4.6. Interestingly, when 0.15 mbar of H₂O was introduced with 0.15 mbar of H₂, little effect on the distribution of Re oxidation states, the binding energy of the Re species, and the Re/Pt ratio at 393 and 473 K was observed. Even when the H₂ was removed and 0.3 mbar H₂O was allowed to react with 8 wt% Pt-Re/C no significant changes in the XPS response of the Re component of the catalyst were detected.

Distribution of Re Oxidation States						
Kinetic Energy	Re(0)	Re(II)	Re(IV)	Re(VII)	Avg. B.E. (eV) ^b	Re/Pt
150 eV	5%	1%	67%	27%	44.2	9.68
500 eV	16%	4%	56%	24%	43.9	5.56
1000 eV	28%	16%	42%	14%	43.3	4.29
1446 eV*	39%	13%	45%	3%	42.6	1.78

Table 4.6: Composition and distribution of Re oxidation states in 8 wt% Pt-Re/C catalyst evaluated by conventional and near-ambient-pressure XPS.

473 K^a

393 K^a

Distribution of Re Oxidation States

Kinetic Energy	Re(0)	Re(II)	Re(IV)	Re(VII)	Avg. B.E. (eV) ^b	Re/Pt
150 eV	31%	9%	39%	21%	43.6	1.36
500 eV	26%	22%	38%	14%	43.9	3.75
1000 eV	53%	6%	33%	7%	42.7	3.58
1446 eV*	59%	11%	31%	0%	42.1	2.21

Room Temperature Before Reduction^b

Distribution of Re Oxidation States

Kinetic Energy	Re(0)	Re(II)	Re(IV)	Re(VII)	Avg. B.E. (eV) ^b	Re/Pt
150 eV**	1%	1%	7%	82%	46.1	2.35
500 eV	1%	1%	41%	57%	45.3	5.63
1000 eV	0%	2%	51%	47%	44.9	4.73
1446 eV*	7%	0%	11%	81%	45.6	1.80

^aMeasurments performed in 0.3 mbar H₂, unless otherwise noted.

^bWeighted average binding energy.

^cMeasurments taken in UHV.

*Measurements using conventional XPS with an Al K α radiation source with a photon energy of 1486.8 eV. Thus since Re has a kinetic energy of approximately 40 eV the resulting photoelectrons have a kinetic energy of approximately 1446 eV. XPS measurements were also performed in UHV after reduction at the specified condition.

**The curve fitting of this measurement also showed 9% of the Re was in the (VI) oxidation state.

Table 4.7: The distribution of Re oxidation states and the Re/Pt atomic ratio from NAP-XPS of 8 wt% Pt-Re/C at 393 and 473 K, a kinetic energy of 150 eV, and 0.3 mbar of pressure.

	Distribution of Re Oxidation States						
Condition	Re (0)	Re(II)	Re(IV)	Re(VII)	Re/Pt		
H_2	5%	1%	67%	27%	9.68		
H ₂ and H ₂ O	9%	4%	71%	16%	3.50		
H_2O	6%	4%	75%	15%	3.51		
$\mathbf{O}_{2}^{\mathrm{a}}$	15%	1%	35%	48%	6.68		

393 K

^aAfter reducing in H₂ at 393 K, the measurement was performed in O₂ at 333 K.

473 K					
	Distri	bution of R	e Oxidation	States	
Condition	Re(0)	Re(II)	Re(IV)	Re(VII)	Re/Pt
\mathbf{H}_2	31%	9%	39%	21%	1.36
H ₂ and H ₂ O	22%	34%	29%	15%	1.62
H ₂ O	27%	23%	34%	15%	1.39

A separate experiment was then performed to test whether oxidation could be observed when a strong oxidant was introduced at a pressure of 0.3 mbar. The catalyst was first reduced at 393 K in situ and an XPS measurement was recorded. The catalyst was then cooled to 333 K, 0.3 mbar of O_2 gas was introduced, and after 20 min a NAP-XPS measurement was obtained. The results of this experiment are summarized in Figure 4.7 and Table 4.7. Severe oxidation of Re occurred at 333 K in the presence of O_2 compared to the reduced catalyst at 393 K. This control experiment indicates that oxidation of the Re did take place with an oxidant at the pressures used for the NAP-XPS technique.



Figure 4.6: Re 4f NAP-XPS of 8 wt% Pt-Re/C at 393 and 473 K, a kinetic energy of 150 eV, and with 0.3 mbar of pressure of either H_2 , H_2 and H_2O , or H_2O . The grey dots are the data and the dotted black lines are the results from peak fitting.



Figure 4.7: Comparison of Re 4f NAP-XPS of 8 wt% Pt-Re/C at 393 in 0.3 mbar of H_2 and at 333 K in O_2 . The grey dots are the data and the dotted black lines are the results from peak fitting.

4.4 Discussion

The extensive characterization of Pt-Re bimetallic nanoparticles revealed that Re exists in a variety of oxidation states when the Pt-Re samples were reduced in H_2 at 473 K or lower. Daniel et al. used X-ray absorption spectroscopy to study Pt-Re bimetallic catalyst supported on Norit Carbon and reported that the Re L_{III} edge energy shift of the

catalyst reduced in H₂ at 473 K corresponded to an average Re oxidation state of approximately +2, which is in general agreement with our XPS results³. The Re L_{III} edge energy shift was also utilized by Koso et al. and Nakagawa et al. to characterize Rh-Re and Ir-Re bimetallic catalysts supported on silica, respectively, and they also reported that the average Re oxidation state was approximately +2 after reduction in H₂ at 393 K^{5,21}.

The Re/Pt atomic ratio, derived from XPS, of the silica-supported catalyst Pt-Re bimetallic catalyst decreased as the catalyst was reduced, indicating that Re segregated from the surface of the catalyst to the core of the catalyst under reducing conditions. Somorjai and co-authors have recently studied the restructuring of the Pt-Pd and Rh-Pd bimetallic systems under different reaction conditions using atomic ratios derived from a near ambient pressure synchrotron based XPS technique similar to that used in this work^{22,23}. The phenomena of Re segregation to the core with reduction at elevated temperatures is consistent with the model proposed by Chia et al. for Rh-Re nanoparticles⁷. In that work, EXAFS results indicated that bimetallic particles with a Re-rich core were formed at high reduction temperatures. Concurrent results from the catalytic hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran showed that the rate decreased with increasing reduction temperature (up to 723 K) indicating that the number of active sites, which most likely require Re, decreased at the surface. The authors used CO chemisorption to rule out metal sintering as a cause for the decreased rate. Rhenium segregation to the core of Pt-Re bimetallic alloys is also consistent with calculations performed by Greely and Mavrikakis, which suggest that as Re/Pt alloys are heated to higher temperatures the most stable configuration consists of subsurface Re with a Pt overlayer²⁴.

4.5 Conclusions

X-Ray photoelectron spectroscopy of Pt-Re bimetallic catalysts was performed with a Conventional ultra-high-vacuum spectrometer and a NAP analyzer equipped with tunable synchrotron radiation. Conventional XPS demonstrated that without a treatment in H₂, Pt was always metallic, however Re was present in an oxidized state. Upon a reduction treatment in H₂ at 393 or 473 K Conventional and NAP-XPS showed that the Re was partially reduced but, a range of Re oxidation states still existed on the surface of the catalyst including Re⁷⁺, Re⁴⁺, Re²⁺, and Re⁰. The presence of Pt also enhanced the reduction of Re because monometallic Re does not reduce until approximately 573 K. Depth profiling of carbon-supported Pt-Re nanoparticles, obtained by changing the kinetic energy of ejected photoelectrons, revealed that metallic Re exists in the core of the nanoparticles while the oxidation of Re increases at the surface. After reduction in 0.3 mbar of H₂ at both 393 and 473 K, NAP-XPS revealed that the presence of 0.3 mbar of H₂O did not change the oxidation state of Re. When 0.3 mbar of O₂ was added to the XPS chamber however, significant oxidation of Re took place, indicating that the low pressure of 0.3 mbar was adequate to cause oxidation of Re.

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Chapter 5: Evidence for a Brønsted Acid Site and Kinetics of Glycerol Hydrogenolysis on Supported Pt-Re Nanoparticles

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5.1 Introduction

While a significant amount of work has documented the performance of bimetallic catalysts consisting of Re together with a platinum group metal, the mechanism of C-O bond hydrogenolysis in liquid water and the promotional role of Re are still unclear^{1–4}. The Tomishige group has studied the hydrogenolysis of different molecules and proposes the role of Re is to act as a Lewis acid. For glycerol hydrogenolysis, they speculate glycerol anchors to the surface through the terminal alcohol group. The C-O bond of glycerol is then thought to be activated by a hydride produced from the heterolytic cleavage of $H_2^{3,4}$.

A different mechanism for hydrogenolysis of oxygenates was proposed by Chia et al¹. In that work, researchers used results from reaction studies, NH₃ temperature programed desorption, and density functional theory (DFT) calculations to suggest that a Brønsted acid site is associated with the Re component of the bimetallic catalyst in liquid water. Supported by results from quantum chemical calculations, Chia et al. suggested that protolytic activation preferentially occurred at the internal carbon of glycerol instead of the terminal carbon because secondary carbenium ions are more stable than primary carbenium

ions¹. Following the acid-catalyzed dehydration of glycerol on the speculated acid site associated with Re, the unsaturated reaction intermediate could then be hydrogenated by the late transition metal component of the catalysts (Rh) to form the final product (1,3-PDO). Consistent with the mechanism involving a Brønsted acid site, the ion formation energies of several other oxocarbenium ions showed a strong correlation with the rate of hydrogenolysis of the corresponding oxygenate¹.

Other works have also suggested that Brønsted acid sites associated with Re are responsible for the increased rate of glycerol APR when Re is added to Pt based catalysts^{5–8}. In addition, FTIR spectroscopy of adsorbed pyridine showed that Brønsted acid sites were present on Pt-Re bimetallic catalysts supported on silica^{5,7}. It is unclear from these studies, however, whether or not Brønsted acid sites are ascribed to the Pt-Re bimetallic nanoparticles or to weakly-held perrhenate species on the silica surface⁹. Ciftci et al. also used evidence from CO stripping voltammetry to show that Re is a strong binder of oxygen species, which could facilitate water activation to produce OH species on the surface⁵.

Li and co-authors have studied glycerol hydrogenolysis extensively using bifunctional catalysts comprised of Pt and different heteropolyacids (HPA) supported on zirconia^{10–13}. They observed a very strong correlation between the number of Brønsted acid sites, measured by the FTIR spectroscopy of adsorbed pyridine, and the yield of 1,3-PDO from glycerol hydrogenolysis at 453 K. Their work suggests that the Brønsted acid sites on the HPA's contribute to the production of 1,3-PDO, presumably by acid-catalyzed dehydration followed by Pt-catalyzed hydrogenation.

In this work, the bifunctional nature of supported Pt-Re bimetallic catalysts is investigated. The Pt-Re system was chosen because theoretical calculations suggest that Pt-Re bimetallic nanoparticles form the strongest Brønsted acid sites (based on deprotonation energy) compared to other bimetallic systems containing a reducible metal and an oxophilic metal^{1,14}. Glycerol hydrogenolysis in the presence of NaOH, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed pyridine, and propyl acetate hydrolysis were used to gain critical insights into the role of the Re component in bimetallic Pt-Re nanoparticles for glycerol hydrogenolysis. In addition, the kinetics of glycerol hydrogenolysis were investigated by varying glycerol concentration and H₂ pressure as well as measuring the kinetic isotope effect using d_5 -glycerol(OH)₃ and D₂.

5.2 Experimental Methods

5.2.1 Polyol Hydrogenolysis

Glycerol hydrogenolysis reactions were performed in a 300 cm³ Parr autoclave equipped with a glass liner, PID-controlled heater, magnetically-driven stir bar, and a dip tube for periodic sampling. The reaction solution was prepared by diluting glycerol (Acros Organics, ACS Grade) with distilled, deionized water. D₂O (Sigma Aldrich, 99.9%), *d5*glycerol(OH)₃ (Cambridge Isotopes Laboratories, 99%) and D₂ gas (Cambridge Isotopes Laboratories, 99.8%) were also used when specified. For the selective poisoning experiments NaOH (Sigma Aldrich) and NaCl (Acros Organics) were dissolved in the reactant solution with glycerol. For a typical reaction, catalyst was loaded into the autoclave and the solution was loaded into a separate reactant vessel that was wrapped with heating tape. The appropriate amount of catalyst was loaded into the empty reactor to give a ratio of moles of glycerol to total moles of Re (Gly/Re) equal to 150. In the experiments where the glycerol concentration was varied a catalyst mass of 160 mg was maintained. After the contents were sealed in their respective containers, H_2 was used to purge the reactor and the reactant solution vessel for 20 min at atmospheric pressure. To re-reduce the catalyst after exposure to air, an in situ reduction was performed at 393 K and 1.4 MPa of H₂ for 1 hour. The reactant vessel was then heated to the reaction temperature of 393 K. When the reactant vessel reached the desired temperature, the solution was charged into the reactor and the reactor was pressurized to the desired pressure with H_2 . An initial sample of the reaction medium was taken through the dip tube while keeping the reactor sealed. The desired pressure of H_2 was maintained throughout the reaction by constantly feeding H₂. Samples were taken periodically throughout the course of the reaction and were analyzed using an Alliance high performance liquid chromatograph (Waters e2695) equipped with a refractive index detector (Waters 2414) and an Aminex ion exclusion column (Bio-Rad, HPX-87H) operating at 318 K with a 0.5 M H_2SO_4 mobile phase. Calibration curves were obtained using known concentrations of reactants and products.

The conversion was calculated as the total moles of products divided initial moles of glycerol and the selectivity for a specific product was the moles of that product divided by the total moles of product. The only products observed for glycerol hydrogenolysis at 393 K with H_2 in the headspace were 1,2-PDO, 1,3-PDO, 1-propanol (1-Prop), and 2propanol (2-Prop) – lactic acid was also observed when high concentrations of NaOH were used. All glycerol hydrogenolysis reactions performed in this work had a carbon balance between 90 and 105%. For simplicity, the ratio of C-O cleavages at secondary carbons versus primary carbons was calculated as the Sec:Prim ratio to compare selectivities for reactions performed with different catalysts. This number was calculated using the concentrations of the final products as shown below.

$$\frac{Sec}{Prim} = \frac{[1,3-PDO] + [1-Prop]}{[1,2-PDO] + 2*[2-Prop] + [1-Prop]}$$

The procedure for hydrogenolysis of 1,2-hexanediol (1,2-HDO) was very similar to that used for glycerol hydrogenolysis. Solutions containing 110 mM of 1,2-HDO (Acros Organics, 98%) in distilled, deionized water or n-heptane (Sigma Aldrich, 99%) were used as the reaction medium. Samples were analyzed using a gas chromatograph (Hewlett Packard 5890 Series II) equipped with a flame ionization detector and a 50 m-long HP-1 cross-linked methyl silicone gum capillary column. Calibration curves were obtained using known concentrations of reactants and products. The Sec:Prim ratio for 1,2-HDO hydrogenolysis was calculated as the ratio of 1-hexanol to 2-hexanol at various points throughout the reaction profile.

5.2.2 Propyl Acetate Hydrolysis

The reactor setup and procedure for propyl acetate hydrolysis were similar to those described in the previous section. The reactant solution for the hydrolysis experiment was prepared by mixing propyl acetate (Sigma Aldrich, 99%) and 1-butanol (Sigma Aldrich, 99.8%) with distilled, deionized water to give 1.5 and 0.1 wt% in propyl acetate and 1-butanol, respectively. The 1-butanol was used as an internal standard. The monometallic Pt and bimetallic Pt-Re catalysts were reduced in situ at 393 K with 1.4 MPa H₂ as described in Section 2.5.1, but after reduction, the reactor was purged four times with N₂

and cooled to the reaction temperature of 333 K. The reactants were then charged to the reactor, which was subsequently pressurized to 2.1 MPa in N₂. Samples were taken throughout the course of the reaction through a dip tube; after each sample, the reactor was backfilled with N₂ to maintain a pressure of 2.1 MPa. Samples were analyzed using a gas chromatograph (Hewlett Packard 5890 Series II) equipped with a flame ionization detector and a 50 m-long HP-1 cross-linked methyl silicone gum capillary column. The conversion was calculated as the moles of 1-propanol formed divided by the moles of propyl acetate initially loaded into the reactor. Response factors were concentrations using known volumes of reactants and products.

The appropriate amount of catalyst was loaded into the reactor in each experiment to ensure the ratio of moles of propyl acetate to total nominal moles of Re (or in the case of HCl, moles of H+) was 100. The HCl (Fisher, Certified ACS Plus) was used as received.

Ethanol was also detected as a side product throughout the course of the propyl acetate hydrolysis experiments. The molar ratio of ethanol to 1-propanol throughout the course of the reaction, performed in N₂, remained constant for 28 h at about 0.1:1. To investigate the evolution of ethanol further, another propyl acetate hydrolysis experiment was also performed in the presence of 2.1 MPa of H₂ on 8 wt% Pt-Re/SiO₂. In this experiment, the ratio of ethanol to 1-propanol was approximately 0.8:1 and the rate of propyl acetate hydrolysis based on 1-propanol production was 3.9 μ mol g⁻¹min⁻¹. In addition, another experiment was performed at the same conditions using acetic acid as the substrate instead of propyl acetate. The rate of acetic acid conversion in this experiment was 15 μ mol g⁻¹min⁻¹. Therefore in the presence of H₂, ethanol is presumably produced

from the direct hydrogenolysis of propyl acetate and the hydrogenolysis of acetic acid, a product of the hydrolysis reaction. Nevertheless, when N_2 is used to fill the head space of the reactor the more than 85% of the propyl acetate conversion can be ascribed to hydrolysis catalyzed by the Brønsted acid associated with the Re component of the Pt-Re catalyst because only a small concentration of ethanol was detected.

5.2.3 Diffuse Reflection Infrared Fourier Transform Spectroscopy (DRIFTS) of Adsorbed Pyridine

The IR spectrum of pyridine adsorbed on the catalysts was recorded on a Bio-Rad FTIR (FTS-60A) spectrometer equipped with a liquid nitrogen cooled MCT detector and an in situ reactor cell for DRIFTS measurements (Harrick). To obtain spectra, 100 scans were co-added at resolution of 2 cm⁻¹. The silica-supported samples used in DRIFTS were diluted in KBr powder (Varian Inc.) to give a 5 wt% catalyst mixture.

The loaded DRIFTS cell was first purged with 28 cm³ min⁻¹ of H₂ for 10 min and then heated to 473 K at a ramp rate of 10 K min⁻¹ and reduced at 473 K in flowing H₂ for 1 h. After the catalyst was reduced, the cell was then purged at 473 K with 20 cm³ min⁻¹ of He for 15 min. Spectral backgrounds were then recorded at 373 and 303 K as the catalyst was cooled in He. At 303 K, a stream of pyridine vapor diluted in He was exposed to the sample for 1 min. The saturator containing pyridine was maintained at a temperature of 273 K. After adsorption of pyridine, the cell was purged with He and the temperature of the cell was increased to 373 K to remove the majority of physisorbed pyridine prior to recording spectra. In separate experiments, a He water mixture was introduced to a reduced catalyst sample via a water saturator maintained at room temperature. The cell was then purged with He for 15 min at 473 K before any backgrounds were recorded after water adsorption.

5.3 Results

5.3.1 IR Spectroscopy of Adsorbed Pyridine

To characterize any Brønsted acid sites associated with the Pt-Re bimetallic nanoparticles, DRIFTS of adsorbed pyridine was used. Pyridine is a strong base that is commonly used to characterize acid sites on solid surfaces using IR spectroscopy because the IR signature of adsorbed pyridine is different when it is associated with a hydrogen bond, a Brønsted acid site, or a Lewis acid site^{11,15–21}. Table 5.1 shows the IR absorption frequencies of the three vibrational modes (8a, 19a, and 19b) that are typically used to study the interaction of pyridine with solid surfaces. In this work, the silica-supported catalysts were used in the DRIFTS experiments because carbon-supported catalysts absorbed the IR radiation.

Spectra of pyridine adsorbed on 8 wt% Pt-Re/SiO₂-W and 8 wt% Pt/SiO₂, collected at 373 K after in situ reduction in H₂ at 473 K, are presented in Figure 5.1. The major peaks at 1597 and 1446 cm⁻¹ are associated with physically adsorbed pyridine, presumably on the silica support^{15–21}. The peak located at 1541 cm⁻¹ in Figure 5.1a is associated with the protonated pyridinium ion and therefore confirms the presence of Brønsted acid sites on 8 wt% Pt-Re/SiO₂-W. A spectrum of the unwashed catalyst showed the same features that can also be ascribed to pyridine bound to a Brønsted acid site. Figure 5.1b confirmed that acid sites were not present on 8 wt% Pt/SiO₂.

	Frequencies (cm ⁻¹)					
Pyridine Interaction	19b	8a	19a			
Physisorbed	1440-1446	1595-1598				
H-Bond	1440-1447	1580-1600				
Brønsted Acid	1540-1550	1640	1489			
Lewis Acid	1440-1464	1610-1630	1481			

Table 5.1: Typical pyridine interactions and their corresponding IR absorption frequencies for the three main vibrational modes.



Figure 5.1: DRIFTS of adsorbed pyridine at 373 K after purging with He for 20 min on a) 8 wt% Pt-Re/SiO₂-W and b) 8 wt% Pt/SiO₂. Spectra are offset for clarity.

Zhang et al. and Ciftci et al. also observed Brønsted acid sites on silica-supported Pt-Re bimetallic catalysts revealed by IR spectroscopy of adsorbed pyridine^{5,7}. In those works, however, the authors reported that the number of Brønsted acid sites increased when

the catalysts were exposed to water vapor prior to pyridine. To investigate the role of water vapor, a DRIFTS experiment was conducted with 8 wt% Re/SiO₂ whereby water vapor was introduced at 473 K before the introduction of pyridine. Figure 5.2 compares the resulting spectrum from this experiment to a spectrum of 8 wt% Re/SiO₂ that was not pretreated with water.



Figure 5.2: DRIFTS of adsorbed pyridine on 8 wt% Re/SiO₂ at 373 K after purging with He for 20 min a) with the addition of water vapor and b) without the addition of water vapor. Spectra are offset for clarity. The spectra in Figure 5.2 suggest that, after reduction in H₂ at 473 K, Re supported

on silica mainly functions as a Lewis acid for pyridine. The result is corroborated by the work of Kawai et al. who observed higher reduction temperatures of Re/Al₂O₃ lowered the ratio of Brønsted acid sites to Lewis acid sites while maintaining the total amount of

adsorbed pyridine²². The spectra in Figure 5.2 also suggest that the addition of water vapor hydrates the supported Re species and converts the Lewis acid sites to Brønsted acid sites. It is possible that catalysts pretreated with water vapor in the works by Zhang et al. and Ciftci et al. converted weakly-held perrhenate species on the silica to Brønsted acid sites rather than converting bimetallic Pt-Re sites, which is why we probed a "washed" catalyst with soluble Re species removed from the surface. Nevertheless, DRIFTS of adsorbed pyridine confirms that Brønsted acid sites are associated with Pt-Re bimetallic particles and the addition of water is not required to form active sites on catalysts reduced at 473 K.

5.3.2 Propyl Acetate Hydrolysis

The hydrolysis of propyl acetate, a well-known Brønsted acid-catalyzed reaction, was used to obtain an estimate of the number of acid sites present on the Pt-Re bimetallic catalysts in liquid water. The hydrolysis of aqueous esters has been commonly used as a probe reaction to characterize other solid acids^{23–25}.

The conversion of propyl acetate was below the detectable limit at 333 K in 2.1 MPa of N_2 after 24 h of reaction in the absence of catalyst. The silica support and the Pt/SiO₂ catalyst did show a low hydrolysis activity, most likely from the few weak acid sites on SiO₂. For example, the conversion of propyl acetate after 24 h of reaction of the silica support was 0.2%, while the conversion on 8 wt% Pt/SiO₂ was slightly lower. The conversion of propyl acetate on 8 wt% Pt-Re/SiO₂ was 4.3% after 24 h, which was significantly higher than the silica support. The rate of propyl acetate hydrolysis remained constant on the bimetallic Pt-Re catalyst over the course of 28 h. Table 5.2 shows the conversions and rates of propyl acetate hydrolysis on 8 wt% Pt-Re/SiO₂ and 8 wt% Pt-Re/SiO₂ was Pt-Re/SiO₂ and 8 wt% Pt-Re/SiO₂ was Pt-Re/SiO₂ and 8 wt% Pt-R

Re/SiO₂-W measured after 8 h of reaction. A plot of the conversion as a function of time is shown in Figure 5.3. The 8 wt% Pt-Re/SiO₂-W catalyst exhibited approximately 60% of the rate of the 8 wt% Pt-Re/SiO₂ catalyst. Interestingly, the same fractional decrease in the rate of glycerol hydrogenolysis was also observed on the washed catalyst compared to the unwashed catalyst (Chapter 3). Evidently, the washing procedure removed about 30 to 40% of the Re sites that are active for both propyl acetate hydrolysis and glycerol hydrogenolysis. The higher propyl acetate hydrolysis rate of the Re-promoted Pt catalyst compared to Pt/SiO₂ supports the hypothesis that Pt-Re bimetallic particles contain acid sites after reduction in H₂ at 393 K, which participate in hydrolysis of propyl acetate at 333 K.

Propyl acetate hydrolysis was also performed with 8 wt% Pt/C and 8 wt% Pt-Re/C (not shown), but the bare Vulcan support had a very high activity, presumably due to surface carboxylic acid groups. Nevertheless, 8 wt% Pt-Re/C still had a higher rate than both the bare Vulcan support and the 8 wt% Pt/C catalyst.

Catalyst	Conversion ^a (%)	Rate (µmol g ⁻¹ min ⁻¹)	H ⁺ Equivalent Per Re
8 wt% Pt-Re/SiO ₂	1.1	1.0	0.10
8 wt% Pt-Re/SiO ₂ -W	0.7	0.6	0.06
HCl (TOF ^b = 0.00039 s^{-1})	11.1	-	1

Table 5.2: The production of 1-propanol from propyl acetate hydrolysis.

Reaction Conditions: 333 K, 2.1 MPa N₂, 8 h of reaction, substrate/Re(H+)=100, 150 cm³ 1.5 wt% propyl acetate solution In situ pretreatment: 393 K, 1.4 MPa H₂, 1 h ^aBased on 1-propanol production ^bBased on total moles of H⁺
To obtain an estimation of the number of Re atoms in the bimetallic catalyst that form acid sites, the rate of hydrolysis on the Pt-Re catalysts was compared to the rate of hydrolysis in aqueous HCl. Thus, a reaction was performed in which the amount of HCl used as a catalyst was equal to the nominal loading of Re used in a typical hydrolysis experiment with Pt-Re bimetallic catalyst. In Table 5.2, the ratio of the propyl acetate conversion on the Pt-Re catalysts to the conversion in aqueous HCl was then used to infer the number of H⁺ equivalents on the Pt-Re catalyst. This measure suggests that approximately 10% of the Re on the unwashed catalyst forms Brønsted acid sites that are active for propyl acetate hydrolysis. Since the acid sites that catalyze hydrolysis on the unwashed catalyst can be attributed to the Pt-Re nanoparticles as well as adsorbed perrhenate, it may be more appropriate to conclude that the H⁺ equivalents measured using 8 wt% Pt-Re/SiO₂-W was a better estimate of acid sites associated with the bimetallic clusters. Our results suggest that at least 6% of the Re on the catalyst forms Brønsted acid sites.



Figure 5.3: Reaction profile for propyl acetate hydrolysis at 333 K on 8 wt% Pt-Re/SiO₂ (\blacklozenge) and 8 wt% Pt-Re/SiO₂-W (\blacksquare). The lines are drawn to guide the eye.

5.3.3 Selective Poisoning of Pt-Re Catalyst

To determine whether the Brønsted acid sites associated with the Re component of the Pt-Re bimetallic catalyst played a role in glycerol hydrogenolysis, the rate of the hydrogenolysis reaction was measured on a 4 wt% Pt-Re/C catalyst in the presence of NaOH. A carbon-supported bimetallic catalyst was chosen for this set of experiments because silica is known to dissolve in aqueous solutions at high pH²⁶. The results from glycerol hydrogenolysis in the presence of different concentrations of NaOH after 2 h of reaction are shown in Table 5.3.

			Selectivities (%)				
Na:Re molar ratio	Conversion (%)	Rate (µmol g ⁻¹ min ⁻¹)	1,2- PDO	1,3-PDO	2-Prop	1-Prop	Sec:Prim
-	8.0	6.8	25	24	13	38	0.69
0.5 5 50	6.5 3.1 3.2	5.3 2.5 2.9	28 81 78	25 19 5	18 0 0	30 0 0	0.59 0.23 0.07*
5	7.8	6.7	23	27	14	36	0.73
50	4.0	3.5	25	32	12	32	0.80
	Na:Re molar ratio - 0.5 5 50 5 50	Na:Re Conversion molar (%) - 8.0 0.5 6.5 5 3.1 50 3.2 5 7.8 50 4.0	Na:Re molar ratioConversion (%)Rate $(\mu mol g^{-1}min^{-1})$ -8.06.80.56.55.353.12.5503.22.957.86.7504.03.5	Na:Re molar ratioConversion (%)Rate ($\mu mol g^{-1}min^{-1}$)1,2- PDO-8.06.8250.56.55.32853.12.581503.22.97857.86.723504.03.525	Na:Re molar ratioConversion (%)Rate ($\mu mol g^{-1}min^{-1}$)1,2- PDO1,3-PDO-8.06.825240.56.55.3282553.12.58119503.22.978557.86.72327504.03.52532	Na:Re molar ratioConversion (%)Rate ($\mu mol g^{-1}min^{-1}$)1,2- PDO1,3-PDO2-Prop-8.06.82524130.56.55.328251853.12.581190503.22.9785057.86.7232714504.03.5253212	Na:Re molar ratioConversion (%)Rate (µmol g ⁻¹ min ⁻¹)1,2- PDO1,3-PDO2-Prop1-Prop- 8.0 6.8 25 24 13 38 0.5 6.5 5.3 28 25 18 30 5 3.1 2.5 81 19 0 0 50 3.2 2.9 78 5 0 0 5 7.8 6.7 23 27 14 36 50 4.0 3.5 25 32 12 32

Table 5.3: Influence of NaOH and NaCl on glycerol hydrogenolysis over 4 wt% Pt-Re/C.

Reaction Conditions: 4 wt% Pt-Re/C, 393 K, 4 MPa H₂, 2 h of reaction, 90 cm³ 110 mM glycerol solution, Gly/Re=50

In situ pretreatment: 393 K, 1.4 MPa H₂ for 1 h

*17% product selectivity to lactic acid was observed

Very small amounts of NaOH decreased the rate of glycerol hydrogenolysis significantly over 4 wt% Pt-Re/C. When a molar ratio of NaOH/Re=0.5 was used, the rate of reaction decreased by 37%. The rate decreased even further when the NaOH/Re molar ratio increased to 5. At 100 mM NaOH, the rate actually increased while the selectivity to 1,3-PDO as well as the Sec:Prim ratio were very low. This increase in rate was attributed to a change in reaction mechanism because of the added base. Other studies have demonstrated base-catalyzed hydrogenolysis of the terminal C-O bonds of glycerol takes place in the presence of Pt at high pH^{27–29}. In 100 mM NaOH, 17% of the product was actually lactate after 2 h of reaction, which also supports the change in reaction path. Clearly, addition of NaOH neutralized the acid sites responsible for activation of glycerol at the secondary carbon and increased the rate of terminal C-O bond activation, thus lowering the Sec:Prim ratio. Nevertheless, a significant decrease in the rate of glycerol hydrogenolysis was observed as the molar ratio of NaOH to Re was increased from 0 to

50, before a significant change in the reaction mechanism was reflected in the rate of reaction or the Sec:Prim ratio.

Additional experiments were performed in which NaCl was added to the reaction mixture in an attempt to decouple the possible influence of Na⁺ on activity and selectivity. As shown in Table 5.3, the reaction with 10 mM NaCl revealed a rate and product selectivity that was approximately the same as the reaction without NaCl, indicating that the catalyst was not negatively affected by the addition of NaCl salt at these conditions. This result also suggests that the 63% decrease in rate observed in the presence of 10 mM NaOH can be attributed to the added presence of OH⁻. Interestingly the rate of glycerol hydrogenolysis decreased from 6.7 to 3.5 µmol g⁻¹min⁻¹ when 100 mM NaCl was added to the reaction medium. It is possible that some of the sodium ions at high concentration exchanged with the acidic protons associated with the Brønsted acid sites created by the Pt-Re bimetallic nanoparticles or that the higher concentration of Cl⁻ may have negatively affected the Pt component of the catalyst, since it is well known that the presence of Cl⁻ can coordinate to platinum group metals and negatively affect the catalytic activity^{27,30,31}. Regardless of the effect on absolute activity, the Sec:Prim ratio remained very high in the presence of NaCl.

In summary, results from the addition of NaOH and NaCl to the reaction medium are consistent with the hypothesis that a Brønsted acid site associated with the Re component of the catalyst is critical in the activation of secondary C-O bonds during glycerol hydrogenolysis on Pt-Re bimetallic catalysts.

5.3.4 Kinetics of glycerol hydrogenolysis on 8 wt% Pt-Re/SiO₂

Figure 5.4 shows rate of glycerol hydrogenolysis measured over a wide range of glycerol concentrations (15 to 550 mM) after 1 h of reaction. The conversions and selectivities for these experiments are presented in Table 5.4. As illustrated in Figure 5.4, the reaction order in glycerol approached zero at high concentrations suggesting that the catalytic surface was nearly saturated with a glycerol-derived species at concentrations above 550 mM. In contrast, the rate of hydrogenolysis was approximately first order in glycerol at low concentrations. Chia et al. studied tetrahydrofurfuryl alcohol hydrogenolysis on a carbon supported Rh-Re catalyst and also reported a first order dependence on tetrahydrofurfuryl alcohol concentration in the range of 94 to 439 mM¹. Tomishige and co-authors, however, observed the rate of tetrahydrofurfuryl alcohol hydrogenolysis on both silica-supported Rh-Re and Ir-Re catalysts³², and the rate of glycerol hydrogenolysis on silica-supported Rh-Re³³ and Ir-Re⁴ catalysts to be zero order in the oxygenates. The studies of cyclic ether and polyol hydrogenolysis in liquid water by Tomishige et al. involved substrate concentrations of approximately 2 M or higher. Thus, the kinetics were most likely measured in the surface saturation regime for both tetrahydrofurfuryl alcohol and glycerol.

In the current work, an interesting trend between the Sec:Prim and the concentration of glycerol was observed Table 5.4. As the concentration of glycerol increased from 15 to 550 mM the Sec:Prim ratio increased from 0.55 to 0.67 indicating that the catalyst was more selective to internal hydrogenolysis reactions at higher concentrations of glycerol.



Figure 5.4: The initial rate of glycerol hydrogenolysis at 393 K and 4 MPa of H_2 in different initial concentrations of glycerol.

Table 5.4: Glycerol hydrogenolysis results at 393 K on 8 wt%	Pt-Re/SiO ₂ after 60
min of reaction with different concentrations of glycerol.	

Concentration (mM)	Time (min)	Conversion (%)	Rate (µmol g ⁻¹ min ⁻¹)	TOF ^a (s ⁻¹)	Sec:Prim
550	60	3.3	164	0.0176	0.67
220	60	6.3	125	0.0134	0.60
110	60	8.9	98	0.0105	0.55
65	60	13.0	64	0.0069	0.54
30	60	12.1	33	0.0035	0.52
15	60	16.3	20	0.0022	0.55

Reaction Conditions: 393 K, 4 MPa H_2 , 90 cm³ solution, 160 mg of 8 wt% Pt-Re/SiO₂ In situ pretreatment: 393 K, 1.4 MPa H_2 for 1 h ^aNormalized by H chemisorption uptake

The order of reaction in H₂ was also investigated for glycerol hydrogenolysis. The H_2 order was measured at three different glycerol concentrations (15, 110, and 550 mM) on 8 wt% Pt-Re/SiO₂. Those results are tabulated in Table 5.5 and summarized in Figure 5.4. At the lowest concentration of glycerol studied (15 mM) the order of H_2 was essentially zero since the rate of glycerol hydrogenolysis was approximately 20 µmol g⁻¹min⁻¹ when the H_2 pressure was varied from 2 to 8 MPa. The observed zero order behavior suggests that saturation coverage of hydrogen is achieved on the Pt-Re catalyst under very low glycerol concentrations. For a reaction in 4 MPa of H₂, the concentration of H₂ in liquid water, based on Henry's Law, is approximately 20 mM which exceeds the concentration of glycerol in solution. The order of reaction in H₂ at higher concentrations of glycerol (110 and 550 mM), however, was quite close to 0.5, which is a result typical of equilibrated dissociative adsorption of H₂ during hydrogenation reactions. Interestingly, the study by Chia et al¹. and the works by Tomishige and co-authors^{32,33} reported first order kinetics in H₂ pressure for cyclic ether and glycerol hydrogenolysis on carbon-supported Rh-Re catalysts and silica-supported Rh-Re and Ir-Re catalysts, respectively. First order behavior in H₂ was not observed during glycerol hydrogenolysis over 8 wt% Pt-Re/SiO₂ under conditions investigated in this work.

A reaction was also performed with N_2 in the head space instead of H_2 with a 110 mM glycerol solution at 393 K. For this experiment, the normal in situ reduction of the catalyst was performed, but prior to adding the reactant solution, the reactor was purged four times with N_2 and then 1 MPa of N_2 was added and maintained throughout the course of the reaction. In the in the absence of added H_2 , the typical glycerol hydrogenolysis

products were still observed (1,2-PDO, 1,3-PDO, 1-Prop, and 2-Prop), even after the catalytic site turned over several hundred times. The reaction with N₂ in the head space, however, also yielded several additional products that were not observed in the presence of H₂, which included acetone, propanal, acetic acid, propanoic acid, and ethanol (observed by GC-MS). Liquid chromatograms for this experiment can be found in Appendix C. The appearance of oxygenates containing carbonyls may be the result of glycerol dehydration. The Brønsted acid-catalyzed dehydration of an alcohol group in glycerol produces an enol, which is rapidly converted in liquid water to a ketone or an aldehyde via keto-enol tautomerization^{34–36}. We suspect that these products are not observed during reactions in high pressure H₂ because of the rapid hydrogenation of these intermediates. Alternatively, glycerol may act both as the substrate and as the source of hydrogen. Other works observed that secondary alcohols can act as the hydrogen source to reduce polyols instead of H₂ following a Meerwein-Ponndorf-Verley reaction mechanism^{37,38}.

The mechanism of glycerol hydrogenolysis was further investigated by probing a kinetic isotope effect with deuterated glycerol, which will be referred to as d5-glycerol(OH)₃. In particular, we measured the rate of hydrogenolysis of glycerol in which all C-H groups were replaced with C-D groups. Using a 15 mM glycerol solution with 4 MPa of H₂, a primary kinetic isotope effect (rate_H/rate_D) of 2.0 ± 0.1 was observed at 393 K. A kinetic isotope effect of approximately 2 was also measured in experiments with 4 MPa of H₂ where the glycerol concentration was 110 and 550 mM. As a control experiment, hydrogenolysis of glycerol (both labeled and unlabeled) was also tested using D₂O as the solvent. No influence of using D₂O instead of H₂O as the solvent was observed. The kinetic

isotope effect of D_2 was also measured using a 15 mM aqueous solution of normal glycerol and 1 MPa of H₂ (D₂) at 393 K. Interestingly, a kinetic isotope effect (rate_H/rate_D) of approximately 0.7 was measured when D₂ was used as the reactant gas, indicating that the rate of glycerol hydrogenolysis was faster with D₂.

Glycerol Concentration (mM)	H ₂ Concentation ^a (mM)	H ₂ Pressure (MPa)	Time (min)	Conversio n (%)	Rate (µmol g ⁻¹ min ⁻¹)	TOF ^b (s ⁻¹)	Sec:Prim
13	40	8	30	7.2	18	0.0019	0.51
	30	6	30	8.0	21	0.0023	0.50
	20	4	30	9.0	22	0.0024	0.51
	10	2	30	9.7	24	0.0026	0.53
110	20	4	60	7.1	73	0.0078	0.53
	10	2	60	5.5	55	0.0059	0.59
	5	1	60	4.8	48	0.0052	0.60
					• • • •		
550	40	8	120	8.2	208	0.0224	0.59
	30	6	120	8.0	197	0.0212	0.61
	20	4	120	6.3	155	0.0167	0.70

Table 5.5: Glycerol hydrogenolysis results at 393 K on 8 wt% Pt-Re/SiO₂ at different pressures of H_2 .

Reaction Conditions: 393 K, 90 cm³ of solution 160 mg of 8 wt% Pt-Re/SiO₂ In situ pretreatment: 393 K, 1.4 MPa H₂ for 1 h

^aCalculated using Henry's Law

^bNormalized by H chemisorption uptake

5.3.5 Polyol hydrogenolysis on 8 wt% Pt-Re/SiO2 in an alkane solvent

To better understand the role of water in the reaction, hydrogenolysis experiments were also performed using alkane (n-heptane) as the solvent. Since the solubility of glycerol in n-heptane is extremely low, 1,2-hexanediol (1,2-HDO) was used as the model polyol substrate because its solubility is relatively high in both water as and n-heptane. The 1,2-HDO hydrogenolysis results over 8 wt% Pt-Re/SiO₂ using water or n-heptane as the solvent are presented in Table 5.6. The observed rate of 1,2-HDO hydrogenolysis was 23 and 48 µmol g⁻¹min⁻¹ in n-heptane and water, respectively, indicating water is not required to perform hydrogenolysis of 1,2-HDO. The rate of 2-hexanol production (2-Hex), which is produced by activating a primary C-O bond in 1,2-HDO, was the same regardless of the solvent used. The rate of 1-hexanol production, on the other hand, was four times higher when water was used as the solvent compared to heptane. The monometallic 8 wt% Pt/SiO₂ catalyst was inactive for 1,2-HDO hydrogenolysis at 393 K in both water and n-heptane indicating that the Re component of the catalyst was crucial for catalysis and the mechanism of 1,2-HDO hydrogenolysis on Pt-Re bimetallic nanoparticles was similar to that of glycerol hydrogenolysis. The results from hydrogenolysis of 1,2-HDO over 8 wt% Pt-Re/SiO₂ also agree very well with work that was previously performed by Nakagawa et al. who studied the hydrogenolysis of 1,2-HDO in n-heptane on Ir-Re/SiO₂³⁹.

				Rate of Production (µmol g ⁻¹ min ⁻¹)			
Solvent	Time (min)	Conversion (%)	Rate (µmol g ⁻¹ min ⁻¹)	TOF ^a (s ⁻¹)	1-Hex	2-Hex	Sec:Prim
Water	120	9.5	48	0.0052	41	7	5.50
n-heptane	240	9.1	23	0.0025	14	8	1.60

Table 5.6: Effect of solvent on hydrogenolysis of 1,2-hexanediol over 8 wt% Pt-Re/SiO₂.

Reaction Conditions: 8 wt% Pt-Re/SiO₂, 393 K, 4 MPa H₂, 110 mM 1,2-HDO solution, Gly/Re=150

In situ pretreatment: 393 K, 1.4 MPa H₂ for 1 h ^aNormalized by H chemisorption uptake

5.4 Discussion

5.4.1 The Nature of the Brønsted Acid Site

Results from this work confirm that Brønsted acid sites are present on the Pt-Re bimetallic catalysts and are most likely associated with the oxophilic Re component, which is consistent with NH₃ temperature programed desorption results suggesting that acid sites are also present on carbon-supported Rh-Re bimetallic catalysts^{1,2}. The DRIFTS spectra in Figure 5.1 indicate that very few Lewis acid sites were present under the conditions of the experiment and nearly all of the acid sites on the silica-supported Pt-Re nanoparticles could be attributed to Brønsted acid sites. These Brønsted acid sites were catalytically active for propyl acetate hydrolysis in liquid water. Since a catalyst that was "washed" to remove soluble perrhenate species weakly-held to the silica support was still active for propyl acetate hydrolysis, we suggest the acid site is attributed to a partially oxidized Re species (Re oxidation state < 7+) associated with Pt. Consistent with the idea that the acid site remains associated with the solid catalyst in liquid water, Chia et al. reported that Rh-Re bimetallic catalysts were active for the acid-catalyzed hydrolysis of fructose to hydroxymethylfurfural in a continuous flow reactor for 250 h².

5.4.2 The Role of Solvent in Hydrogenolysis on Pt-Re Catalysts

The results from this work also shed light on the role of water in glycerol hydrogenolysis. Pyridine DRIFTS showed that the addition of water is not required for Brønsted acid sites to be present on Pt-Re bimetallic nanoparticles. In addition, the NAP-XPS revealed that the addition of 0.3 mbar of water vapor does not change the oxidation state or binding energy of Re in the reduced catalyst indicating that water does not react

with or electronically alter the Re component of the catalyst significantly after the catalyst is reduced in H₂ at temperatures of 473 K and below (Chapter 4). Moreover, the rate of glycerol hydrogenolysis was unchanged when D₂O was used as the solvent instead of H₂O. The hydrogenolysis of 1,2-HDO in an alkane also solvent confirms that water is not required to perform the selective hydrogenolysis of polyols.

5.4.3 Bifunctional Mechanism of Glycerol Hydrogenolysis on Pt-Re Catalysts

The extensive characterization of Pt-Re catalysts confirms that both metallic sites (associated with Pt) and acid sites (associated with partially oxidized Re) are present of the surface of the catalyst. One question that persists is the extent at which the acid site plays a role in the hydrogenolysis mechanism. For example, Chia et al. propose that the Brønsted acid sites selectively catalyze activation at secondary C-O bonds over primary C-O bonds (compared to metal-catalyzed hydrogenolysis) because secondary carbenium or oxocarbenium ions are more stable¹. Indeed, acid-catalyzed dehydration of the secondary carbon of glycerol may form an unsaturated reactive intermediate that would be subsequently hydrogenated on Pt metal sites.

A competing mechanism is the direct hydrogenolysis of glycerol adsorbed on Pt-Re. The direct hydrogenolysis mechanism, favored by the group of Tomishige et al., suggests the heterolytic cleavage of H_2 on Pt-Re sites is involved in the reaction^{3,4}.

Our work on the hydrogenolysis of d5-glycerol(OH)₃ revealed a primary kinetic isotope effect (rate_H/rate_D) of 2.0 ± 0.1 in liquid water indicating that the activation of C-H bonds in glycerol is kinetically significant, which is consistent with the acid-catalyzed path described above. We should also note that C-H bond activation is also a proposed step in the metal-catalyzed hydrogenolysis of glycerol over Pt^{40} , Ru^{40} , and Rh^{41} catalysts. Therefore, the kinetic isotope effect observed with *d5*-glycerol(OH)₃ cannot unambiguously discriminate between acid-catalyzed versus metal-catalyzed C-H bond activation during glycerol hydrogenolysis. Nevertheless, the observed primary kinetic isotope effect with *d5*-glycerol(OH)₃ does not support a hydrogenolysis mechanism involving heterolytic cleavage of H₂ followed by the direct addition of hydrogen to activate C-O bonds in glycerol.

Chia et al. used quantum chemical calculations to show that a low energy path for glycerol hydrogenolysis over Rh-Re bimetallic catalysts is initiated by the protonation of an alcohol group by the Brønsted acid site of the catalyst.¹ Simultaneous with the elimination of water, is an intramolecular hydride shift from a C-H bond on the adjacent CH₂-OH group to form an oxocarbenium ion (RCH-C=O(+)H), which was claimed to be the most stable intermediate. The presence of an alcohol group at the β -carbon position lowered the reaction barrier by 14 kJ mol⁻¹ by providing a back-side stabilization of the transition state. Moreover, the presence of water, in conjunction with the alcohol at the β -carbon, further aided in stabilizing the oxocarbenium ion transition state¹.

Interestingly, we observed that both the rate of hydrogenolysis and the Sec:Prim ratio was lower when n-heptane was used as the solvent instead of water for the hydrogenolysis of 1,2-HDO. The presence of water may help to stabilize the oxocarbenium ion in the transition state of the concerted mechanism while n-heptane cannot provide the back-side stabilization. This might explain why the rate of 1-hexanol production increased by a factor of three when water was used as the solvent instead of n-heptane in the hydrogenolysis of 1,2-HDO.

The order of reaction in both glycerol and H_2 at different glycerol concentrations also provides insights into the glycerol hydrogenolysis mechanism. As mentioned in Section 5.3.4, the orders of reaction have been reported elsewhere in the literature on similar catalysts, but the results are inconsistent. The kinetic analysis summarized in Figure 5.4 suggests that various orders can be found, depending on the conditions used.

Reaction kinetics that were measured in low concentrations of glycerol (15 - 65 mM) show that the reaction is first order in glycerol concentration and approximately zero order in H₂ pressure. In this regime, the surface appears to be saturated with enough hydrogen that perhaps hydrogenation is not kinetically significant and the acid-catalyzed activation and dehydration of glycerol is rate determining. The reported turnover frequency (TOF) of hydrogenation of various carbonyl compounds on Pt catalysts at temperatures as high as 393 K is significantly greater than the rate of glycerol hydrogenolysis observed in this work⁴². In addition, the observed inverse kinetic isotope effect (rate_H/rate_D=0.7) when D₂ was used as the reactant gas with a 15 mM glycerol solution suggests that the hydrogenation step may be equilibrated^{43,44}. Meemken et al. measured a normal kinetic isotope effect (rate_H/rate_D=1.4) with D₂ gas when studying the hydrogenation of a ketone on an alumina-supported Pt catalyst, confirming D₂ should produce a normal kinetic isotope effect when hydrogenation is a kinetically significant step⁴⁵.

At higher concentrations of glycerol, where glycerol approaches zero order behavior, an approximately half order dependence on the H_2 pressure was observed. In this

case hydrogenation of an adsorbed unsaturated intermediate formed by the acid-catalyzed dehydration of glycerol may be kinetically significant. In classical hydrogenation kinetics on late transition metals, half order dependence in H_2 corresponds to equilibrated adsorption of H_2 on a surface catalyzing hydrogen addition reactions. For exclusively metal-catalyzed glycerol hydrogenolysis reactions, the kinetically significant C-H bond activation step may result in a negative influence of H_2 pressure on the rate⁴⁰. Indeed, the initial rate of glycerol hydrogenolysis over Pt^{40} and Rh^{41} was lower in H_2 relative to that in He or N_2 .

In summary, the results presented in this work are consistent with a mechanism in which glycerol hydrogenolysis proceeds via acid-catalyzed dehydration followed by hydrogenation of the resulting unsaturated intermediate.

5.5 Conclusions

Infrared spectroscopy of adsorbed pyridine on Pt-Re/SiO₂ confirmed that Brønsted acid sites were present on the bimetallic nanoparticles after reduction in H₂. These sites were also active for propyl acetate hydrolysis in liquid water. By normalizing the rate of propyl acetate hydrolysis on Pt-Re/SiO₂ to the rate in HCl, we concluded that approximately 6% of the Re associated with the Pt-Re nanoparticles form Brønsted acid sites. The importance of the Brønsted acid sites in glycerol hydrogenolysis was confirmed by the addition of only 10 mM of NaOH to the reaction medium with a carbon-supported Pt-Re catalyst, which decreased the rate of glycerol hydrogenolysis by 60%. The NaOH evidently neutralizes the Brønsted acid sites associated with the Re component of the catalyst. A primary kinetic isotope effect was also observed when *d5*-glycerol(OH)₃ was used as the substrate, indicating the kinetic significance of C-H bond breaking in the glycerol hydrogenolysis mechanism. The characterization and reactivity results confirm the bifunctional nature of Pt-Re bimetallic catalysts and support a hydrogenolysis reaction path that involves acid-catalyzed dehydration followed by metal-catalyzed hydrogenation.

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Chapter 6: Aqueous-Phase Hydrogenation of Saturated and Unsaturated Ketones and Aldehydes over Supported Pt-Re Catalysts

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6.1 Introduction

The selective hydrogenation of C=C and C=O bonds in α , β -unsaturated ketones and aldehydes, such as methyl vinyl ketone (MVK) and crotonaldehyde, has been widely studied for applications in the pharmaceutical, cosmetics, and food industries^{1–5}. Selective hydrogenation of the C=O bond over the C=C bond to obtain unsaturated alcohols is preferred, but the hydrogenation of aliphatic C=C bonds is thermodynamically favored, and typically kinetically favored, over C=O bonds. Therefore, catalysts must be designed to kinetically-control the hydrogenation of C=O bonds over C=C bonds^{2,5}.

Monometallic transition metal catalysts have very high activity for hydrogenation reactions, but have very high selectivity to the undesired saturated aldehydes and ketones². Several bimetallic formulations increase the selectivity to the desired unsaturated alcohol^{3,6–9}. Tin is one of the most common transition metal promoters for hydrogenation reactions and has been shown to increase the selectivity and activity for the hydrogenation of several α,β -unsaturated aldehydes on Pt and Ru based catalysts. For example, the addition of Sn to Pt increase the turnover frequency (TOF) of crotonaldehyde

hydrogenation by over twelve times and increased the selectivity of crotyl alcohol from close to zero on a Pt catalyst to over 40% on a Pt-Sn catalyst⁷. Calvagno et al. demonstrated that a positive correlation existed between the Sn/Ru ratio of carbon-supported bimetallic nanoparticles and the rate of cinnamaldehyde hydrogenation⁹. The addition of Fe to Pt catalysts has been observed to have a similar effect as Sn addition^{10,11}.

The promotional effects of metallic additives like Sn and Fe are explained in two ways. When Sn is added to Pt, Pt^{δ} -Sn^{δ^+} ensembles are formed^{6,7,12}, and the polarity between the two metals increases the binding energy of C=O allowing the C=O bond to be selectively hydrogenated. Concepción et al. used infrared spectroscopy to suggest that a unique carbon monoxide adsorption mode is present on Pt impregnated into Sn-Beta, which may facilitate the adsorption of aldehydes onto a bimetallic ensemble allowing the bond to be more easily activated by hydrogen⁶. Additionally, X-ray photoelectron spectroscopy (XPS) revealed that surface Sn was still oxidized even after a reduction at 623 K supporting the existence of Sn with a partial positive charge⁷. A second explanation for the promotional effect argues that the addition of Sn dilutes Pt ensembles that are highly active for C=C bond cleavage^{3,7}. Passos et al. demonstrated with results from microcalorimetry experiments that the integral heats of adsorption of H₂ and CO on Pt-Sn/Al₂O₃ were approximately the same as on Pt/Al₂O₃¹³, which suggests that the heat of adsorption of aldehyde groups may be the same on Pt-Sn catalysts as on Pt³. Even though the addition of Sn to Pt and Ru has been shown to increase the selectivity of unsaturated aldehyde hydrogenation to unsaturated alcohol, Sn addition does not appear to increase the selectivity of unsaturated ketone hydrogenation to unsaturated alcohols^{2,12}.

Increasing the selectivity of unsaturated aldehyde hydrogenation to unsaturated alcohols has also been achieved by supporting late transition metals on reducible supports. Dandekar et al. demonstrated that titania-supported Pt promoted the rate and the selectivity of crotonaldehyde hydrogenation only when the catalyst was reduced above 773 K¹⁴. It is well known that when reducible supports like titania are reduced at high temperatures, TiO_x species can migrate onto the late transition metal nanoparticles and interact more strongly with the platinum group metal¹⁵. Dandekar et al. attributed the increase in rate and selectivity of crotonaldehyde hydrogenation to Pt metal-interfacial titania sites. The coordinatively-unsaturated Ti cations can interact more strongly with the C=O bond in crotonaldehyde, which increases the rate of reaction and selectivity to crotyl alcohol¹⁴.

Recently, the Tomishige group has reported that the addition of Re to an Ir-based catalyst increased the conversion of crotonaldehyde hydrogenation and the resulting selectivity to crotyl alcohol above 90%¹⁶. The monometallic Re catalyst was essentially inactive at 303 K and 8 MPa of H₂ and the selectivity to crotyl alcohol over monometallic Ir was approximately 60%. Tamura et al. ascribe the increased conversion and selectivity to crotyl alcohol over Ir-Re to the ability of the catalysts to perform the heterolytic cleavage of H₂¹⁶. It has also been hypothesized that the heterolytic cleavage of H₂ explains the high rate and selectivity of polyol (C-O bond) hydrogenolysis over catalysts containing Re and a platinum group metal^{17,18}. The Ir-Re^{19,20}, Rh-Re^{17,21,22}, and Pt-Re²³ bimetallic systems exhibit high rates of polyol hydrogenolysis and high selectivity for the activation of secondary C-O bonds. Interestingly, when the Ir-Re, Rh-Re, Pt-Re, Pd-Re, and Ru-Re

systems were evaluated for the hydrogenation of crotonaldehyde by Tamura et al., only the Ir-Re system had higher conversion and selectivity compared the monometallic catalysts¹⁶.

Work presented in Chapter 5 on the hydrogenolysis of polyols over Pt-Re suggests that the high rates and selectivities of glycerol hydrogenolysis are explained by a bifunctional mechanism in which the protolytic activation of alcohols, by a Brønsted acid site associated with the Re component of the catalyst, is followed by the rapid hydrogenation of the unsaturated intermediate, which contain either a C=C or C=O bond, on the Pt component of the catalyst²⁴. For glycerol hydrogenolysis over Pt-Re, the order in H₂ was measured to be 0.5 at high glycerol concentrations. In classical hydrogenation kinetics on late transition metals, half order dependence in H₂ corresponds to equilibrated adsorption of H₂ on a surface catalyzing hydrogen addition reactions. Thus, understanding the kinetics of C=C and C=O bond hydrogenolysis over bimetallic catalysts consisting of an early and a late transition metal.

In this chapter, the rate of hydrogenation of molecules containing C=O and sometimes C=C bonds was investigated. The hydrogenation rate was normalized to H uptake, measured via H_2 chemisorption, the surface average particle size, obtained via TEM, and total metal atoms, to better quantify the effect of Re on Pt-catalyzed rates. In addition, several experiments were performed to evaluate the significance of mass transfer limitations on the measured conversion to ensure rate measurements were obtained in the kinetically-controlled regime.

6.2 Experimental Methods

6.2.1 Catalyst Preparation

All catalysts were prepared by incipient wetness impregnation of metal precursors followed by a thermal treatment. The Pt-Re bimetallic catalysts were synthesized by successive impregnation of the Pt precursor followed by the Re precursor. The platinum precursor was Pt(NH₃)₄(NO₃)₂ (Sigma Aldrich) and the Re precursor was NH₄ReO₄ (Sigma Aldrich). For a typical catalyst preparation, the Pt precursor was dissolved in a predetermined amount of distilled, deionized water to cause the silica gel support (Fuji Silysia G6) to reach incipient wetness. After the Pt solution was slowly added and thoroughly mixed with the support, the catalyst was dried overnight at 393 K in air. The Re precursor was then dissolved in water and the second impregnation was performed in the same manner. The resulting catalyst was then dried overnight in air at 393 K.

Before any measurements or reactions were performed, the bimetallic and monometallic catalysts were heated to the 723 K and reduced for 3 hours in 100 cm³ min⁻¹ of flowing H₂ (GTS Welco, 99.999%). A passivation gas (GTS Welco, 1.03% O₂ balance N₂) was introduced to the catalysts for 30 min after being cooled to room temperature. Following the gas treatment, the catalysts were stored in air at room temperature in a closed vial.

6.2.2 Catalyst Characterization

The total number of hydrogen adsorption sites was determined by H_2 chemisorption using a Micromeritics ASAP 2020 automated adsorption analyzer. Samples were first heated at 4 K min⁻¹ and reduced at 473 K in flowing H_2 for 1.5 h. Next, the samples were evacuated for 2 h at 473 K and then for another 2 h at 308 K. After the evacuation, analysis was performed at 308 K in the pressure range of 75 to 450 Torr. The total number of hydrogen adsorption sites was calculated by extrapolating the total amount of H₂ adsorbed in the saturated region to zero pressure to remove contributions from physisorbed hydrogen. Transmission electron microscopy (TEM) images of the catalysts were acquired with an FEI Titan operated at 300 kV and equipped with a Gatan 794 Multi-scan Camera and an energy dispersive spectrometer for elemental X-ray analysis. Samples for microscopy were prepared by dipping TEM grids into a mixture of approximately 50 mg of catalyst and 7 cm³ of cyclohexane, which was sonicated for 15 min. To evaluate the particle size of the sample, the diameter of over 300 individual particles was measured for each sample.

6.2.3 Hydrogenation Reactions

Hydrogenation reactions were performed in a 100 cm³ Parr autoclave equipped with a glass liner, PID-controlled heater, Teflon-lined magnetically-driven stir bar, and Teflonlined dip tube for periodic sampling. The reaction solution was prepared by diluting methyl vinyl ketone (Acros Organics, 95%), 2-butanone (Sigma Aldrich, 99.7%), crotonaldehyde (Aldrich, 99%), or butanal (Fluka, 99.0%) with distilled, deionized water and an internal standard. The internal standards 1-propanol and 1-pentanol were used for the ketones and aldehydes, respectively. For a typical reaction, 10 mg of catalyst (unless otherwise stated) was loaded into the autoclave and the solution was loaded into a separate reactant vessel. After the contents were sealed in their respective containers, H₂ was used to purge the reactor and the reactant solution vessel for 10 min at atmospheric pressure. To re-reduce the catalyst after exposure to air, an in situ reduction was performed at 393 K and 15 psig of H₂ for 1 hour. After reduction the reactor was cooled to 333 K, the solution was then charged into the reactor, the reactor was pressurized to 15 psig with H₂, and the magnetically-driven stir bar was set to 650 rpm. An initial sample of the reaction medium was taken through the dip tube while keeping the reactor sealed. The desired pressure of H₂ was maintained throughout the reaction by constantly feeding H₂. Samples were analyzed using a gas chromatograph (Hewlett Packard 5890 Series II) equipped with a flame ionization detector and a 50 m-long HP-1 cross-linked methyl silicone gum capillary column. The conversion was calculated as the moles of products formed divided by the moles of substrate initially loaded into the reactor. Response factors were obtained using known concentrations of reactants and products. All reactions had a carbon balance between 90 and 105%.

6.2.4 Glycerol Hydrogenolysis Reactions

The reactor set-up and procedure for glycerol hydrogenolysis were similar to those used for the hydrogenation reactions. The reaction solution was prepared by diluting glycerol (Acros Organics, ACS Grade) with distilled, deionized water. The appropriate amount of catalyst was loaded into the empty reactor to give a ratio of moles of glycerol to total moles of Re (Gly/Re) equal to 150. After the in situ reduction at 393 K, the reactant vessel was then heated to the reaction temperature of 393 K. When the reactant vessel reached the desired temperature, the solution was charged into the reactor and the reactor was pressurized to the desired pressure with H₂. Samples were taken periodically throughout the course of the reaction and were analyzed using an Alliance high performance liquid chromatograph (Waters e2695) equipped with a refractive index detector (Waters 2414) and an Aminex ion exclusion column (Bio-Rad, HPX-87H) operating at 318 K with a 0.5 M H₂SO₄ mobile phase. Calibration curves were obtained using known concentrations of reactants and products.

The conversion was calculated as the total moles of products divided initial moles of glycerol. The only products observed during glycerol hydrogenolysis at 393 K were 1,2propanediol, 1,3-propanediol, 1-propanol, and 2-propanol. All glycerol hydrogenolysis reactions performed in this chapter had a carbon balance between 90 and 105%. For simplicity, the ratio of C-O cleavages at secondary carbons versus primary carbons was calculated as the Sec:Prim ratio to compare selectivities for reactions performed with different catalysts. This number was calculated using the concentrations of the final products as shown below.

$$\frac{Sec}{Prim} = \frac{[1,3-PDO] + [1-Prop]}{[1,2-PDO] + 2*[2-Prop] + [1-Prop]}$$

6.3 Results and Discussion

6.3.1 Catalyst Characterization

The Pt and Re weight loadings, H_2 chemisorption results, and particle size analysis from TEM for the silica-supported catalysts used in this chapter are provided in Table 6.1. The 8 wt% Pt-Re catalyst was extensively characterized and tested for a number of reactions in Chapters 3-5. In Table 6.1, the H/Pt ratio is a measure of the exposed Pt atoms per total Pt atoms. For supported monometallic Pt catalysts the particle size (in nm) can be estimated from the inverse of H/Pt yielding an average particle size of 2.2 and 3.3 nm for the 4 wt% Pt and 8 wt% Pt catalysts, respectively²⁵. A relationship between H/Pt and average particle size is not well known for the Pt-Re catalyst however, because the average number of adsorbed hydrogen atoms to surface Re atoms in these samples is unknown. Daniel et al. observed that there was no hydrogen uptake for a monometallic Re catalyst supported on Norit carbon in which the average Re oxidation state was measured to be 7+ from X-ray absorption spectroscopy²³. Characterization of the Pt-Re catalyst revealed that the average Re oxidation state for the silica-supported Pt-Re catalyst is between 2+ and 4+, and it is unknown whether hydrogen spillover from surface Pt to surface Re can occur on these materials²⁴. Nevertheless, for the Pt-Re catalysts listed in Table 6.1, the H₂ chemisorption results likely give an estimation of the exposed Pt.

Catalyst	Pt ^a (wt%)	Re ^a (wt%)	H uptake ^b (µmol/g)	H/Pt ^b	Average Diameter ^c (nm)	Surface Average Diameter ^d (nm)
1 wt% Pt	1.0	-	41	0.84	1.7 ± 0.75	2.5
4 wt% Pt	4.0	-	92	0.45	2.0 ± 1.0	3.2
8 wt% Pt	8.0	-	122	0.30	3.5 ± 2.3	8.0
1 wt% Pt-Re	1.0	0.9	41	0.80	1.9 ± 0.56	2.3
2 wt% Pt-Re	2.0	1.9	75	0.73	2.3 ± 0.85	3.1
4 wt% Pt-Re	4.0	3.6	100	0.49	1.8 ± 0.76	2.5
8 wt% Pt-Re	8.0	7.6	172	0.42	1.6 ± 0.59	2.1

Table 6.1: The metal weight loadings, results from H₂ chemisorption, and TEM analysis of silica-supported Pt, Re, and Pt-Re catalysts.

^aNominal weight loadings

 $^b\mbox{Obtained}$ via H_2 chemisorption at 308 K after the catalysts were reduced in situ at 473 K $^c\mbox{Obtained}$ via TEM

^dObtained via TEM by $\Sigma d^3/\Sigma d^2$

Particle size analysis via TEM revealed that the average particle size and the standard deviation for the particle size distribution for the Pt-Re catalysts did not change as a function of metal weight loading. The local density of metal particles simply increased

for higher weight loadings of Pt and Re, as revealed in Figures 1c and 1d. The 8 wt% Pt catalyst, however, had a significantly higher average particle size and standard deviation than the other catalysts studied in this chapter. Some particles as large as 20 nm were observed on the 8 wt% Pt sample (not shown) whereas the largest particles observed in the other samples studied were only as large as ~7 nm. The large particle size for 8 wt% Pt was a result of the high metal loading, which increases the likelihood of sintering during catalyst pretreatment. The 8 wt% Pt-Re catalyst had a smaller average particle size than monometallic 8 wt% Pt since the addition of Re increases the stability of Pt and mitigates sintering²⁶. Deng et al. synthesized a number of Pt-Re catalyst with a molar ratio of unity supported on carbon nanotubes having weight loadings of Pt from 1 to 30%²⁷. Similar to our results, the average particle size measured by TEM increased from 1.5 nm on a 1 wt% Pt-Re catalyst to only 2.3 nm on a 5 wt% Pt-Re catalyst²⁷. The 30 wt% catalyst, however, had an average particle size of 4.9 nm²⁷. Interestingly, characterization with XPS by Deng et al. revealed that the surface Pt to Re ratio was approximately unity for the low-weightloaded catalysts, but Pt became more enriched at the surface for higher weight loadings²⁷.

An electron micrograph of a monometallic Re catalyst did not contain a narrow distribution of particle sizes as observed with the Pt and Pt-Re catalysts (not shown). Instead, TEM images revealed a bimodal distribution consisting of extremely large particles, as large as 50 nm in diameter, and smaller particles roughly 4 to 6 nm in diameter. In addition, very few particles with sufficient contrast were observed for the 4 wt% Re catalyst and a reliable average particle size could not be obtained. Characterization of a silica-supported monometallic Re catalyst synthesized with incipient wetness impregnation

of aqueous metal precursor suggests that Re is weakly held and highly dispersed on silica²⁸. In the current chapter, the resolution of the TEM was not sufficient to observe atomicallydispersed Re, which explains the low number of particles observed.



Figure 6.1: Transmission electron micrographs of a) 1 wt% Pt b) 8 wt% Pt c) 1 wt% Pt-Re d) 8 wt% Pt-Re.

6.3.2 Hydrogenation of C=C bonds in methyl vinyl ketone and crotonaldehyde

The potential influence of H_2 mass transfer limitations in the batch reactor were first evaluated by studying the hydrogenation of MVK over monometallic Pt, which consumed H₂ at the fastest rate for any reaction in this chapter. The rates of MVK hydrogenation normalized to H uptake sites (TOF_H), rates normalized to the amount of total surface metal atoms, calculated from the inverse of the surface average particle size from TEM (TOF_{SM}), as well as the global rate per total amount of metal are listed in Table 6.2 for the monometallic Pt catalysts at 333 K. Reliable rates can be obtained at the high levels of conversion listed in Table 6.2 because the hydrogenation of MVK is typically zero order in the substrate over transition metal catalytsts². Figure 6.2 shows the reaction profiles of MVK hydrogenation over the Pt and Pt-Re catalysts. The rate of reaction did not change as the reaction approached 100% conversion in MVK, which confirms the zero order behavior. The tabulated rates of MVK hydrogenation in Table 6.2 were approximately the same when 10 mg of 1 wt% Pt, 4 wt% Pt, or 8 wt% Pt were used. In addition, 20 mg of the 8 wt% Pt, which converted 56.6% of the MVK after 30 min of reaction, had the same normalized rate of MVK hydrogenation as 10 mg of 8 wt% Pt, confirming that external mass transfer effects were not present in the system. The small change in rate (approximately 30%) as the amount of metal in the reactor varied by a factor of approximately 16 indicates that external and internal mass transfer limitations were not affecting the measured rates²⁹.

The selectivity of MVK hydrogenation for the monometallic Pt catalyst in Table 6.2 also did not change significantly for different Pt loadings. About 99% of the product

was the saturated ketone (SK) formed by hydrogenating the C=C bond. The remaining product was the saturated alcohol (SA), which is a result of the sequential hydrogenation of the SK as depicted in Scheme 1. Production of the unsaturated alcohol (UA) was below the detectable limit for MVK hydrogenation over Pt. Ide et al., who studied the hydrogenation of MVK over a carbon-supported Pt catalyst in liquid water, also did not observe the production of the UA and their selectivies to SK and SA agree well with the results in Table 6.2^2 . The rates for MVK hydrogenation in liquid water presented in Table 6.2 are also similar to the TOF (normalized by H₂ chemisorption) of 0.94 s⁻¹ reported by Ide et al.². The difference between TOF_H and TOF_{SM} in Table 6.2 can be ascribed to a discrepancy between the techniques used to measure active sites. It is possible that atomically-dispersed Pt or metal particles less than 0.4 nm may be present on the silicasupported catalysts, which would not be detected by TEM analysis due to the resolution limitation of the technique. Thus, the true surface average particle size may be smaller than that measured by TEM, which would decrease the TOF_{SM} in Table 6.2 and make it more comparable to the TOF_H.

Ide et al. studied the hydrogenation of MVK over carbon-supported Pd, Pt, Ru, and Au catalysts and did not report the formation of UA regardless of the metal used. This result was explained using quantum chemical calculations for the reaction occurring on a Ru (0001) surface². For the most stable adsorption mode of MVK on Ru (0001), the molecule is parallel to the surface so bonding can occur through both the C=O and C=C bonds with four Ru atoms. After coordination through this planar η^4 mode, hydrogen can then add to either carbon in the adsorbed C=C moiety in addition to the carbon or oxygen

atom in the ketone group. Results from quantum chemical calculations presented by Ide et al. showed that addition of hydrogen to the carbon atom of the carbonyl had the lowest barrier of each of the four possible atoms. The secondary carbon in the C=C bond had the next lowest barrier for the initial hydrogen addition. The lower barrier for the carbonyl carbon was ascribed to the enhanced stabilization of the transition state by the strong Ru-O bond. The addition of a second hydrogen can then occur on the C=C bond to create the intermediate for the SK or the C=O bond to form the UA. The activation barrier to add the initial hydrogen to the C=O bond was 10 kJ mol⁻¹ lower than the addition to the C=C bond, but this is not reflected in the selectivity trends over Ru or Pt, in which over 95% of the product is the SK because the barriers of desorption for the intermediate leading to the UA (-113 kJ mol⁻¹) is significantly higher than the desorption barrier for the SK intermediate (-28 kJ mol⁻¹) over Ru (0001).

The work by Ide et al. highlighted the difficulty in selectively hydrogenating unsaturated ketones to the unsaturated alcohols with monometallic catalysts². In fact, reports of metal catalysts selectively hydrogenating MVK to the UA are very few³⁰. The production of UA from MVK, however, has been demonstrated with homogeneous borohydrides^{4,31} and over MgO^{4,32}. In the case of MgO, hydrogen was not supplied with molecular hydrogen but with a hydrogen donor molecule, such as 2-propanol. Magnesia was able to form the UA with high selectivity (69% at 78% conversion) since the barriers to adsorb C=C bond to MgO are very high³². To the best of our knowledge the Pt-Re catalyst has not yet been tested for this reaction, however, and it is possible that the presence of oxophilic Re on the surface may preferentially adsorb the C=O bond.

						Selectivities (%)		
Catalyst	Mass Catalyst (mg)	Conversion (%)	${{{\rm TOF}_{{\rm H}}}^{\rm a}} \over {({\rm s}^{-1})}$	TOF _{SM} ^b (s ⁻¹)	Rate $(\mu mol g_{metal}^{-1}s^{-1})$	SK	SA	UA
1 wt% Pt	10	21	0.54	1.1	2300	100	0	0
4 wt% Pt	10	22	0.52	0.75	1200	99	1	0
8 wt% Pt	10	18	0.49	1.2	750	99	1	0
8 wt% Pt	20	57	0.43	1.0	660	97	3	0

Table 6.2: Testing the mass transfer limitations of MVK hydrogenation over monometallic Pt at 333 K

Reaction Conditions: 333 K, 15 psig H_2 , 45 cm³ of 0.2 M aqueous MVK solution In situ pretreatment: 393 K, 15 psig H_2 for 1 h ^aNormalized by H chemisorption uptake

^bNormalized by surface metal atoms (Pt + Re) evaluated from the inverse of the average particle size obtained from TEM

The results of MVK hydrogenation over the Pt-Re catalysts are presented in Table 6.3. The TOF_{SM} of MVK hydrogenation over 1 wt% Pt-Re agrees well with the TOF's reported in Table 6.2 for the monometallic Pt catalyst. As the metal weight loadings increased, the TOF_H, TOF_{SM}, and the rate per total amount of metal for MVK hydrogenation appeared to decrease over the Pt-Re catalysts. As displayed in Figure 6.1, nanoparticles on the low-weight-loaded Pt-Re catalyst sparsely populate the silica support. Since the average particle size of 1 wt% Pt-Re and 8 wt% Pt-Re are essentially the same, it logically follows that the nanoparticles on 8 wt% Pt-Re would be very densely populated as confirmed in Figure 6.1d. It is well known that Re can be highly dispersed on metal oxide supports like silica²⁸ and it is possible that a larger percent of the Re is more widely dispersed on the silica support in 1 wt% Pt-Re than 8 wt% Pt-Re and not associated with Pt nanoparticles. In other words, Re is more likely to cover Pt hydrogenation sites on 8 wt% Pt-Re compared to 1 wt% Pt-Re, since the nanoparticles are more densely packed at high weight loadings. Consistent with this idea, H₂ chemisorption measured a higher
fraction of exposed Pt on 1 wt% Pt-Re than 8 wt% Pt-Re and in general, as the Pt-Re weight loading increased the fraction of Pt exposed decreased (Table 6.1). Thus, the lower rate of MVK hydrogenation over the high-weight-loaded Pt-Re catalysts can be ascribed to Re blocking Pt hydrogenation sites. As observed in Table 6.3, the addition of Re does not appear to change the selectivity of MVK hydrogenation.



Figure 6.2: Conversion during MVK hydrogenation over monometallic Pt and bimetallic Pt-Re catalysts.

Appreciable selectivity to the UA can more easily be obtained during the selective hydrogenation of unsaturated aldehydes like crotonaldehyde (Scheme 2). Marinelli et al. were able to obtain 13% selectivity to the unsaturated alcohol in the gas phase over a Pt/SiO₂ catalyst³³ and Ide et al. demonstrated that it is possible to obtain a selectivity as high as 37% to crotyl alcohol in liquid water over an Au/C catalyst². Using a silica-supported Ir catalyst, Tamura et al. achieved 63.7% selectivity to the unsaturated alcohol

at 5.4% conversion of crotonaldehyde¹⁶. The methyl group next to the C=O bond in MVK apparently inhibits the selective hydrogenation of MVK to the UA, but the low steric hindrance near the C=O bond in crotonaldehyde evidently improves the selectivity of crotyl alcohol from crotonaldehyde hydrogenation^{2,4}.



Scheme 6.1: Reaction network for MVK hydrogenation

Tamura et al. observed that when a silica-supported Ir catalyst was promoted by Re, the selectivity of crotonaldehyde hydrogenation to the UA was as high as 92.0% at 43.0% conversion¹⁶. Table 6.4 shows that only a moderate increase in the selectivity to the UA was achieved, however, when Re was used to promote silica-supported Pt, with the highest selectivity to UA reaching 21%. In general, the selectivity to the UA appeared to increase as the Pt-Re metal weight loading increased. Similar to MVK hydrogenation, the overall rate of crotonaldehyde hydrogenation over the Pt-Re catalyst was comparable to the rate over the monometallic Pt catalyst, and the TOF_{SM} and rate per total amount of metal for crotonaldehyde hydrogenation appeared to decrease has the Pt-Re weight loading increased. The slower rate of crotonaldehyde hydrogenation compared to MVK

hydrogenation over Pt is ascribed to the steric hindrance of the C=C bond in crotonaldehyde by the methyl group^{2,4,33}. Nevertheless, the TOF_H for 4 wt% Pt/SiO₂ agrees closely with the TOF of 0.13 s⁻¹ reported by Ide et al. at similar conditions.

					Selectivities (%)		s (%)
Catalyst	Conversion (%)	${{{\rm TOF}_{{ m H}}}^{ m a}}$ (s ⁻¹)	TOF _{SM} ^b (s ⁻¹)	Rate (µmol g _{metal} ⁻¹ s ⁻¹)	SK	SA	UA
1 wt% Pt-Re	30	1.2	1.2	2700	99	1	0
2 wt% Pt-Re	19	0.70	0.80	1300	99	1	0
4 wt% Pt-Re	19	0.50	0.31	660	99	1	0
8 wt% Pt-Re	30	0.37	0.16	410	98	2	0

Table 6.3: Reaction results for the hydrogenation of MVK over Pt-Re catalysts with different weight loadings of metal and a Pt to Re molar ratio of unity

Reaction Conditions: 333 K, 15 psig H_2 , 45 cm³ of 0.2 M aqueous MVK solution In situ pretreatment: 393 K, 15 psig H_2 for 1 h

^aNormalized by H chemisorption uptake

^bNormalized by surface metal atoms (Pt + Re) evaluated from the inverse of the surface average particle size obtained from TEM

Tamura et al. explained the increased selectivity to UA during crotonaldehyde hydrogenation over Ir-Re catalyst by speculating the presence of Re causes the heterolytic cleavage of H₂, leading to the selective activation of polar C=O bonds. Hydride addition to C=O bonds by homogeneous metal hydride complexes has been reported in the literature^{34–37}. The addition of Re or Mo to late transition metals was also claimed to lower the barrier to heterolytically activate H₂ to form a hydride that selectivity attacks polar bonds, such as the C-O bond in glycerol^{17,38}. Alternatively, the increased rate of glycerol (C-O bond) hydrogenolysis upon the addition of Re to Pt catalyst was discussed in terms of a bifunctional mechanism in which a Brønsted acid associated with the Re component of the catalyst protolytically activates the alcohol of glycerol²⁴. Nevertheless, hydride addition

catalyzed by the Re component of the catalyst may explain the selective hydrogenation of C=O bonds.



Scheme 6.2: Reaction network for crotonaldehyde hydrogenation

Reyes et al. observed that the selectivity during cinnamaldehyde hydrogenation to cinnamyl alcohol increased from 70% over Rh/SiO₂ to almost 100% over a Rh-Mo/SiO₂ catalyst³⁹. Characterization of the Rh-Mo catalysts using XPS revealed several Mo oxide species and a Rh^{δ +} species that was only observed in the presence of Mo. The promotion of Rh by Mo was thought to result in a Rh^{δ +}-MoO_x species, which was responsible for the increased selectivity to the UA³⁹. As mentioned earlier, the presence of coordinatively-unsaturated Ti cations has also been invoked to explain the increased selectivity to the UA during crotonaldehyde hydrogenation over Pt/TiO₂ and Ni/TiO₂ that were reduced at adequately high temperatures to initiate the migration of Ti species onto the Pt or Ni particles¹⁴. Our characterization of the Pt-Re catalysts using XPS indicated Pt was

essentially all metallic, although there was a measurable shift for the core levels of surface

					Selectivities (%)		
Catalyst	Conversion (%)	TOF_{H}^{a} (s ⁻¹)	TOF _{SM} ^b (s ⁻¹)	Rate $(\mu mol g_{metal}^{-1}s^{-1})$	SAL	SA	UA
4 wt% Pt	2.5	0.082	0.12	190	92	3	5
1 wt% Pt-Re	1.4	0.13	0.12	270	82	8	10
2 wt% Pt-Re	2.3	0.075	0.085	140	86	7	7
4 wt% Pt-Re	2.7	0.092	0.056	120	69	11	20
8 wt% Pt-Re	4.6	0.081	0.036	89	74	5	21

Pt to higher binding energy in the presence of Re^{24} .

Table 6.4: Reaction results for the hydrogenation of crotonaldehyde over Pt-Re catalysts after 30 min of reaction with different weight loadings of metal and a Pt to Re molar ratio of unity

Reaction Conditions: 333 K, 15 psig H_2 , 45 cm³ of 0.2 M aqueous crotonaldehyde solution, 50 mg of catalyst

In situ pretreatment: 393 K, 15 psig H_2 for 1 h

^aNormalized by H chemisorption uptake

^bNormalized by surface metal atoms (Pt + Re) evaluated from the inverse of the surface average particle size obtained from TEM

Even though a significant level of electron sharing was not detected in Pt-Re nanoparticles using XPS, we ascribe the increase in the UA selectivity for crotonaldehyde hydrogenation to the preferential adsorption of the C=O bond onto the oxophilic Re component of the Pt-Re bimetallic catalyst. The MVK hydrogenation results indicate that Re more extensively blocks Pt sites on the high-weight-loaded Pt-Re catalysts, which is also consistent with the selectivity trends in crotonaldehyde hydrogenation. The high-weight-loaded Pt-Re catalysts exhibited higher selectivity to UA than the low-weight-loaded Pt-Re catalysts.

The results in Table 6.4 were obtained after 30 min of reaction because significant deactivation of the catalysts was observed during the hydrogenation of crotonaldehyde over Pt and Pt-Re. Figure 6.3 shows the conversion of crotonaldehyde during hydrogenation as

a function of time over 10 mg of the Pt-Re catalysts and 10 mg of the 4 wt% Pt catalyst. Deactivation, as indicated by the decrease in the slope of the curve, was significant over 4 wt% Pt and the low-weight-loaded Pt-Re catalysts. The 8 wt% Pt-Re catalyst did not appear to deactivate as quickly. A significant level of deactivation was not observed during the hydrogenation of MVK over these catalysts (Figure 6.2). Englisch et al. also observed deactivation during the hydrogenation of crotonaldehyde in liquid water over Pt/SiO2⁴⁰. They found that the initial rate of hydrogenation was able to be restored by a treatment of the used catalyst in air⁴⁰. When 40 mg of 1 wt% Pt-Re was used as the catalyst, however, the deactivation behavior was similar to the 8 wt% catalyst. Apparently, the deactivation rate is related to the catalyst/substrate ratio, which suggests a poisoning species may be present in the crotonaldehyde feed. Nevertheless, the rate of hydrogenation after 30 min of reaction for 10 or 40 mg of 1 wt% Pt-Re was approximately the same, suggesting that the poison did not significantly affect the rate of reaction at short reaction times.

Since the product selectivity consisted predominately of the SK and the SAL for the hydrogenation of MVK and crotonaldehyde, respectively, the overall hydrogenation rates presented in Tables 3 and 4 are mainly associated with the rate of C=C bond hydrogenation. To understand the kinetics of glycerol hydrogenolysis, the hydrogenation of C=O bonds is likely to be more relevant because a hypothetical intermediate that may be formed following the dehydration of glycerol is most likely a ketone (or aldehyde) since the equilibrium associated with keto-enol tautomerization in liquid water is shifted away from the enol^{41–43}. Bohne et al. measured the [keto]/[enol] equilibrium constant of propanal and butanal in liquid water at 328 K to be 1.3×10^5 and 1.8×10^5 , respectively⁴². In addition, the rate of tautomerization to acetone at 328 K in liquid water reported by Chaing et al.⁴¹ was approximately 70 s⁻¹, which is significantly faster than both C=C and C=O bond hydrogenation, indicating that upon the formation of the proposed enol intermediate during glycerol hydrogenolysis, it will rapidly tautomerize to the keto (or aldehyde) form.



Figure 6.3: Conversion during crotonaldehyde hydrogenation over monometallic Pt and bimetallic Pt-Re catalysts. The mass of catalyst was 10 mg unless otherwise stated.

6.3.3 Hydrogenation of C=O bonds in 2-butanone and butanal

To study the rate of C=O bond hydrogenation in the absence of C=C bonds, the hydrogenation of 2-butanone to 2-butanol and butanal to 1-butanol was evaluated over Pt and Pt-Re. The results for 2-butanone hydrogenation are presented in Table 6.5. As seen with both MVK and crotonaldehyde hydrogenation, the TOF_{H} and TOF_{SM} of 2-butanone

hydrogenation over the low-weight-loaded Pt-Re catalyst was similar to that of 2-butanone hydrogenation over a monometallic Pt catalyst. In the case of 2-butantone, however, upon increasing the weight loading of Pt-Re, which likely increased the Re/Pt ratio at the surface of the nanoparticles, the TOF_H of 2-butanone hydrogenation increased by a factor of approximately 5 (see Table 6.5). While the higher Re content on the surface appears to decrease the rate of C=C bond hydrogenation (as shown with MVK and crotonaldehyde), the rate of 2-butanone hydrogenation and the selectivity trends for crotonaldehyde hydrogenation in Table 6.4 suggest that more Re on the surface promotes the rate of C=O bond hydrogenation.

Table 6.5: Reaction results for the hydrogenation of 2-butanone over 4 wt% Pt and the Pt-Re catalysts

Catalyst	Conversion (%)	TOF _H ^a (s ⁻¹)	TOF _{SM} ^b (s ⁻¹)	Rate (µmol g _{metal} ⁻¹ s ⁻¹)
4 wt% Pt	2.9	0.0036	0.0052	8.3
1 wt% Pt-Re	0.7	0.0053	0.0050	11
2 wt% Pt-Re	1.6	0.0081	0.0092	16
4 wt% Pt-Re	3.8	0.014	0.0088	18
8 wt% Pt-Re	10	0.029	0.013	32

Reaction Conditions: 333 K, 15 psig H_2 , 45 cm³ of 0.2 M aqueous 2-buantone solution, 50 mg of catalyst, 1 h In situ pretreatment: 393 K, 15 psig H_2 for 1 h ^aNormalized by H chemisorption uptake

^bNormalized by surface metal atoms (Pt + Re) evaluated from the inverse of the average particle size obtained from TEM

*The product selectivity was 100% to the saturated alcohol

In Table 6.6, the results from the hydrogenation of butanal to 1-butanol are presented after 1 h of reaction. Results are presented after the same reaction time because deactivation was observed, similar to that found in crotonaldehyde hydrogenation as illustrated in Figure 6.3. The results of butanal hydrogenation over the low-weight-loaded catalysts were not reported because reliable levels of conversion were not obtained after 1 h of reaction. Comparison of the rates of 2-butanone hydrogenation (Table 6.5) and butanal hydrogenation (Table 6) over monometallic Pt indicates hydrogenation of the aldehyde is substantially faster than the ketone. The TOF_H of but and hydrogenation over the highweight-loaded Pt-Re catalysts was slightly higher than that over the monometallic Pt catalyst, which agrees with results from 2-butanone hydrogenation as reported in Table 6.5. Unlike the case with 2-butanone, no discernable trend in TOF_{SM} or global rate with the weight loading of metals was observed with butanal. In fact, the rate of butanal hydrogenation did not seem to be affected by the interaction between Pt and Re as significantly as the other molecules studied (MVK, crotonaldehyde, and 2-butanone). Thus, the interaction of Pt and Re enhances the rate of C=O bond hydrogenation more strongly when the C=O bond is a sterically-hindered ketone compared to when the C=O bond is an aldehyde. It is possible that the oxophilic Re increases the preferential adsorption of the ketone, but the expected increased adsorption strength of the aldehyde, which is not sterically hindered, is apparently less pronounced.

Catalyst	Conversion (%)	TOF _H ^a (s ⁻¹)	TOF _{SM} ^b (s ⁻¹)	Rate $(\mu mol g_{metal}^{-1}s^{-1})$
4 wt% Pt	2.2	0.016	0.023	37
4 wt% Pt-Re	3.4	0.038	0.024	50
8 wt% Pt-Re	3.7	0.032	0.014	35

Table 6.6: Reaction results for the hydrogenation of butanal over 4 wt% Pt and the Pt-Re catalysts

Reaction Conditions: 333 K, 15 psig H_2 , 45 cm³ of 0.2 M aqueous butanal solution, 30 min In situ pretreatment: 393 K, 15 psig H_2 for 1 h

^aNormalized by H chemisorption uptake

^bNormalized by surface metal atoms (Pt + Re) evaluated from the inverse of the average particle size obtained from TEM

*The product selectivity was 100% to the saturated alcohol

A summary of the C=C and C=O bond hydrogenation results observed for MVK, crotonaldehyde, and 2-butanone over different weight-loaded Pt-Re catalyst is depicted in Figure 6.4. Over the low-weight-loaded catalyst, the rates of C=C and C=O bond hydrogenation were similar to those over monometallic Pt. The low-weight-loaded Pt-Re catalyst had a higher fraction of exposed silica support causing Re to preferentially reside on the silica instead of on the Pt nanoparticles. Thus, the undecorated Pt particles exhibited a catalytic performance similar to monometallic Pt. The Pt-Re nanoparticles on the highweight-loaded Pt-Re catalysts, however, were more densely packed on the silica support evidently resulting in more intimate mixing of Pt and Re, which created bimetallic ensembles. The decoration of Re on the Pt nanoparticles blocked Pt sites that catalyzed C=C bond hydrogenation resulting in lower rates of MVK and crotonaldehyde hydrogenation over the high-weight-loaded Pt-Re catalysts (Tables 3 and 4) relative to monometallic Pt. The presence of oxophilic Re in close contact with Pt on the high-weightloaded catalysts enhanced the rate of C=O hydrogenation in 2-butanone. The Re may have facilitated the preferential adsorption of C=O in 2-butanone leading to an increased rate of hydrogenation by hydrogen spillover from the Pt component of the catalyst. The increased selectivity to the UA during crotonaldehyde hydrogenation appeared to be the result of selective inhibition of C=C hydrogenation by Re without inhibiting C=O hydrogenation. For the 8 wt% Pt-Re catalyst, the hydrogenation TOF_H for crotonaldehyde (which was a measure of mostly C=C bond hydrogenation) and butanal (which was a measure C=O bond hydrogenation) was approximately the same, 0.036 and 0.032 s⁻¹, respectively, which

explains the enhanced selectivity of crotonaldehyde hydrogenation to the unsaturated alcohol upon the addition of Re.



Low Weight Loaded Catalysts Rates of C=C and C=O bond hydrogenation over Pt-Re were similar to those over Pt

High Weight Loaded Catalysts Re covering Pt lowers rate of C=C bond hydrogenation and increases rate of C=O bond hydrogenation (in ketone)

Figure 6.4: Schematic representation of Pt-Re catalysts used for hydrogenation.

6.3.4 Implications for Glycerol Hydrogenolysis over Pt-Re

The rate and selectivities during glycerol hydrogenolysis at 393 K were also measured over the Pt-Re catalysts with varying metal weight loadings, as reported in Table 6.7, confirming that all of the Pt-Re catalysts were active for glycerol hydrogenolysis. A monometallic Pt catalyst was essentially inactive at the conditions used. The results in Table 6.7 reveal that selectivity (indicated by the Sec:Prim ratio, which is measure of selectivity explained in Section 2.4) was not a function of the Pt-Re metal loading. As discussed earlier, the TOF_{SM} and global rate of C=C bond hydrogenation appeared to decrease with increasing Pt-Re weight loading (Table 6.3 and 6.4), which differs from the trend in glycerol hydrogenolysis rates reported in Table 6.7. The TOF_H for glycerol hydrogenation in 2-butanone. In other words, the highest TOF_H for glycerol hydrogenolysis and 2-butanone hydrogenation were both observed on the 8 wt% Pt-Re catalyst.

Catalyst	Conversion (%)	TOF_{H}^{a} (s ⁻¹)	TOF _{SM} ^b (s ⁻¹)	Rate (µmol g _{metal} ⁻¹ s ⁻¹)	Sec:Prim
1 wt% Pt-Re	5.4	0.0029	0.0027	6.2	0.44
2 wt% Pt-Re	8.6	0.0049	0.0056	9.4	0.57
4 wt% Pt-Re	6.9	0.0066	0.0035	7.5	0.47
8 wt% Pt-Re	6.9	0.0083	0.0030	7.5	0.57

Table 6.7: The rate and selectivities of glycerol hydrogenolysis over the Pt-Re catalysts

Reaction Conditions: 393 K, 4 MPa H_2 , 90 cm³ 110 mM glycerol solution, Gly/Re=150 In situ pretreatment: 393K, 1.4 MPa H_2 for 1 h

^aNormalized by H chemisorption uptake

^bNormalized by surface metal atoms (Pt + Re) evaluated from the inverse of the surface average particle size obtained from TEM

The rates for 2-butanone and butanal hydrogenation at 333 K over 8 wt% Pt-Re were substantially greater than the rate of glycerol hydrogenolysis at 393 K. This comparison suggests that the rates of C=O (and C=C) bond hydrogenation at the conditions for glycerol hydrogenolysis would be much faster than the rate of hydrogenolysis since the activation energy for C=O bond hydrogenation has been measured to be greater than 40 kJ/mol over transition metal catalysts^{44,45}. The rapid rate of hydrogenation relative to hydrogenolysis is consistent with a mechanism of hydrogenolysis in which glycerol dehydration, catalyzed by a Brønsted acid site, is a kinetically significant step and that subsequent hydrogenation is fast²⁴.

6.4 Conclusions

The rates of C=C and C=O bond hydrogenation in MVK, crotonaldehyde, 2butanone, and butanal in liquid water were measured over Pt and Pt-Re catalysts supported on silica in the kinetically-controlled regime. The normalized rate of MVK and crotonaldehyde hydrogenation, which involves primarily C=C bond hydrogenation, decreased as the metal weight loading of Pt-Re catalyst with a 1:1 nominal Pt:Re ratio increased. Results from H₂ chemisorption and TEM suggest that the high-weight-loaded Pt-Re catalysts had a relatively higher ratio of Re to Pt at the surface compared to the low-weight-loaded Pt-Re catalysts. Consistent with that observation, the rates of MVK and crotonaldehyde hydrogenation over monometallic Pt were similar to those over the low-weight-loaded Pt-Re catalyst. In contrast, the rate of C=O bond hydrogenation in 2-butanone was higher for the high-weight-loaded Pt-Re catalysts compared to monometallic Pt. For crotonaldehyde hydrogenation, the addition of Re adjusted the relative rates of C=C and C=O bond hydrogenation thereby increasing the selectivity to unsaturated aldehyde from 6% over Pt to 21% over Pt-Re. The same Pt-Re catalysts were also tested for glycerol hydrogenolysis in liquid water. The relative rates of C=C and C=O bond hydrogenation over Pt-Re were significantly faster than C-O bond hydrogenolysis, supporting they hypothesis that a hydrogenation step in the glycerol hydrogenolysis mechanism would be kinetically irrelevant.

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Chapter 7: Concluding Remarks

7.1 Conclusions

The substantial increases in the selectivity of glycerol hydrogenolysis upon the addition of Cu to Ru catalysts and Re to Pt catalysts were investigated. The addition of Cu to Ru increased the selectivity of glycerol hydrogenolysis to 1,2-PDO from approximately 50% on the monometallic Ru catalyst to over 90% on the Ru-Cu catalyst. In general as the Cu/Ru ratio increased, the selectivity to 1,2-PDO increased while the rate based on surface Ru atoms only decreased slightly. It was concluded that Cu diluted Ru ensembles that are highly active for C-C bond activation reactions. The addition of Cu did not negatively affect the rate of dehydrogenation over the catalyst however, causing the selectivity to 1,2-PDO to increase.

The addition of Re to Pt shifts the selectivity from predominantly 1,2-PDO towards the production of both 1,2-PDO and 1,3-PDO. The promotion of Re also increases the rate of glycerol hydrogenolysis by several orders of magnitude at 393 K. Extensive characterization using two different XPS techniques revealed that Pt was always in the metallic state after a thermal treatment in H₂ at 723 K, to synthesize the catalyst, but Re was oxidized when it is exposed to air. After in situ reduction of Pt-Re catalyst in H₂ at 393 or 473 K the Re became partially reduced since Pt catalyzed the reduction of Re, but a range of Re oxidation states were still present on the surface. Near ambient pressure XPS also revealed that the presence of 0.3 mbar of water vapor did not alter the oxidation state of the partially reduced Re subjected to the in situ reduction.

It was also confirmed that a Brønsted acid site was associated with the Re component of the catalyst using DRIFTS of adsorbed pyridine. Propyl acetate hydrolysis was used to probe the activity of the Brønsted acid site in liquid water. Normalizing the rate of hydrolysis over Pt-Re to the rate in homogeneous HCl it was approximated that 6% of the Re atoms form Brønsted acid sites. When the Brønsted acid sites were selectively poisoned by introducing NaOH to the glycerol hydrogenolysis reaction mixture, the rate of hydrogenolysis and selectivity to 1,3-PDO was negatively affected indicating that the Brønsted acid site plays a crucial role in the reaction mechanism. In addition, glycerol hydrogenolysis experiments conducted with monometallic silica-supported Pt and homogeneous acid suggest that close contact between the Pt and the Brønsted acid site is required to obtain high rates of glycerol hydrogenolysis.

A mechanism involving the protolytic cleavage of the secondary alcohol in glycerol by the Brønsted acid site followed by the Pt metal-catalyzed hydrogenation of the unsaturated intermediate was proposed to explain the promotional effect of Re. Hydrogenolysis experiments with deuterated glycerol produced a primary kinetic isotope effect suggesting that dehydration of glycerol involving C-H bond activation is involved in a kinetically significant step in the reaction mechanism. The reaction order in H_2 and an inverse kinetic isotope effect when dideuterium gas was used as the reactant gas also supports a hydrogenolysis mechanism involving Brønsted acid catalyzed hydration and does not support a mechanism in which the metal catalyzes the direct hydrogenolysis of glycerol.

The rate of C=C bond hydrogenation in methyl vinyl ketone and crotonaldehyde, normalized to both H_2 chemisorption uptake and total surface metal, was approximately the same over low weight loaded Pt-Re catalysts as the monometallic Pt catalysts. Bimetallic Pt-Re catalysts with high metal weight loadings, however, had a lower activity for C=C bond hydrogenation. Dihydrogen chemisorption analysis of Pt-Re catalysts suggested that the surface Re/Pt ratio for catalysts with high metal weight loadings was greater than the catalysts with low metal weight loadings. It was concluded that the presence of Re decreased the rate of C=C bond hydrogenation by breaking up Pt ensembles. The addition of Re to the Pt catalyst increased the rate of C=O bond hydrogenation in 2butanone, however, presumably because the presence of oxophilic Re increased the binding energy through the oxygen in the sterically-hindered ketone. Since the rate of C=C bond hydrogenation was significantly faster than the rate of C=O bond hydrogenation in both MVK and crotonaldehyde, the addition of Re changed the product distribution for crotonaldehyde hydrogenation only slightly and did not affect the MVK product distribution. The 8 wt% Pt-Re catalyst exhibited the highest turnover frequency of 2butanone hydrogenation. In fact, the turnover frequency, based on H uptake, for glycerol hydrogenolysis was the highest over 8 wt% Pt-Re. The rate of 2-butanone hydrogenation at 333 K was approximately the same as the rate of glycerol hydrogenolysis at 393 K indicating that hydrogenation of both C=C and C=O bonds will be kinetically insignificant at the conditions for glycerol hydrogenolysis.

The Pt-Re bimetallic catalyst has a range of unique properties. This work demonstrates that Pt-Re is an active catalyst for hydrogenolysis, hydrogenation, hydrolysis, and dehydration in liquid water, which are important reactions in the processing of molecular-derivatives from biomass.

7.2 Future Work

7.2.1 Quantification of Surface Re

Throughout the catalysis literature it is common to normalize conversion to the number of active sites, which is measured using a technique such as chemisorption, to obtain a rate per active site. In this dissertation, the rate of reaction was obtained by normalizing the conversion, in both hydrogenolysis and hydrogenation reactions, to either H₂ uptake sites, total nominal metal loading, or total surface metal estimated from TEM. These surface measurements however, are surrogates for the true quantity of active sites because we are unable to measure the active sites exclusively.

For example, in Chapter 3 we have shown that H_2 chemisorption may not be the best way to measure the rate of glycerol hydrogenolysis in liquid water since no trend was observed between the rate per catalyst mass and the H_2 chemisorption uptake. Therefore, to increase our understanding of the Pt-Re catalyst, and all bimetallic catalyst containing Re and a late transition group metal, a probe molecule to measure surface Re exclusively needs to be developed. Typical chemisorption probes, such as H_2 and CO, do not measure Re adequately because Re is not able to activate H_2 by itself and CO will bind to both Re and Pt. To complicate matters further, X-ray photoelectron spectroscopy results presented in Chapter 4 show that the Pt and Re are highly mobile within the catalytic particle and the ratio on the surface changes depending on the reducing or oxidizing potential of the environment to which the catalyst is subjected. Therefore, an operando measurement of Pt and/or Re dispersion, if possible, may yield more information about the surface participating in catalysis.

Additional characterization with in situ X-ray techniques such as X-ray photoelectron spectroscopy and X-ray absorption spectroscopy may also yield more information about the composition of the Pt-Re particles under different conditions. We obtained a very limited understanding of how the environment changed the composition of the Pt-Re particles, since we were only able to obtain a limited amount of data points. Additionally, by changing the support, the mobility and the behavior of Pt and Re was altered. Therefore, further interrogation of Pt-Re bimetallic nanoparticles needs to be performed to understand how the surface properties are tuned under different conditions.

7.2.2 Understanding the Role of the Platinum Group Metal in Hydrogenolysis

Reactions

Based on results currently available in the literature, the Pt-Re, Rh-Re, and Ir-Re systems all produce high rates and selectivities for glycerol hydrogenolysis, but the catalytic performance of all three of these systems appears to be different. Results from X-ray absorption spectroscopy suggests that Re is present in approximately the same average oxidation state in all three of these systems and the platinum group metal is in the metallic state. Therefore, there is currently a lack of experimental evidence to explain the different

performance in these systems. To study this question further, the number and strength of acid sites present on these catalysts needs to be carefully measured using a basic probe molecule, such as pyridine, and a more complete study of the rate of C=O and C=C bond hydrogenation on these different systems may be required.

7.2.3 Development of Pt-Re Catalysts for Other Reactions and Industrial Applications

Extensive characterization of the Pt-Re catalyst in this work has shown that both an acid (associated with partially oxidized Re) and a metal (Pt) are in close contact on the catalytic surface. Future tasks include the application of this catalyst to other reactions. One biomass relevant reaction that has not been evaluated on Pt-Re is the hydrodeoxygenation of cellobiose. The Brønsted acid can activate the β -linkages to break apart the molecule into sugar monomers. Then, both the acid and metal can activate the alcohol groups on the sugar. Understanding the kinetics and reaction engineering challenges associated cellobiose and Pt-Re (or any other catalysts with an oxophilic and late transition metal) may elucidate solutions for the processing of cellulosic biomass.

The development of the Pt-Re catalyst for industrial applications also needs to be investigated to apply the principles researched herein to large scale challenges. The first step in developing an industrially relevant Pt-Re catalyst is to transition to a flow reactor, which requires choosing a support that does not have a high pressure drop while maintaining the high activity and selectivity of Pt-Re. Once an adequate support and flow reactor design is engineered an extensive study of the stability of the Pt-Re catalyst must be performed before scale up can be recommended.

Appendix A: A Study of Glycerol Hydrogenolysis over Ru-Cu/Al₂O₃ and Ru-Cu/ZrO₂ Catalysts

This chapter is a manuscript submitted to Chemical Engineering Journal and is related to the work presented in Chapter 2: A. V. H. Soares, J. B. Salazar, D. D. Falcone, F. A. Vasconcellos, R. J. Davis, and F. B. Passos. "A study of glycerol hydrogenolysis over Ru-Cu/Al₂O₃ and Ru-Cu/ZrO₂ catalysts."In this work, I obtained the TEM images, performed the H₂ chemisorption, and assisted in interpreting the data.

A.1 Introduction

The search for alternative energy sources has arisen because of concerns related to the environmental impact of using fossil resources. Although the discovery of new oil and natural gas sources can postpone the complete depletion of fossil resources, the problems associated with a shortage are expected to occur within the next few decades. In this context, the quest for sustainability has become an important point in the motivation of academic and industrial scientists and government officials in the planning and development of using renewable biomass as alternative fuels to mitigate the problem. Much of the chemical industry uses oil as the main feedstock in the production of fine chemicals, polymers, and fuels. Nowadays, there is considerable interest to generate power from biomass as well as convert it into chemicals and value-added materials¹.

Biodiesel is a high quality fuel produced by the transesterification of triglycerides, derived from renewable sources like plant oils and animal fats. This biofuel is a liquid with similar combustion properties to diesel oil but it is essentially sulfur free, which makes it more environmentally friendly². Mixing 2 to 30 % biodiesel into fossil derived diesel does

not require changes to engines, and will produce lower amounts of particulate matter³. Biodiesel has been produced on an industrial scale in Europe since 1992 encouraged by institutions and a growing public concern for the environment. In 2012, biodiesel production in Europe reached 8.6 million tons, which is slightly lower compared to previous years⁴. In Brazil, federal legislation⁵ has driven a compulsory biodiesel demand, by enforcing a minimum 5% biodiesel content in all diesel fuel consumed in the country. This has led to an increase in the number of authorized production units and actual biodiesel production. As of February 2014, the total regulated monthly production of biodiesel in Brazil was 243,670 m³, which represents only 37 % of the total authorized capacity in the country. In light of this, production growth is still expected. The Brazilian biodiesel production comes mainly from soybean oil (70.9%) and bovine fat (24.8%)⁶.

For every 9 kg of biodiesel produced, about 1 kg of glycerol is formed as a byproduct. Although there are many applications for glycerol, its production has exceeded the demand, which leads to a depreciation in the value of the product⁷.

In this context, the search for economic and environmentally useful alternatives for glycerol becomes imperative, in order to ensure the continuity and viability of biodiesel production⁸. Among the promising techniques that have been developed for glycerol usage are: hydrogenolysis to produce 1,2- or 1,3-propanediol; aqueous and gas phase reforming to form CO and H₂; etherification reaction to form polyglycerols; and selective oxidation to produce ketones, acids and aldehydes⁹⁻¹¹.

Glycerol conversion by catalytic hydrogenation or hydrogenolysis to glycols, i.e. 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), and ethylene glycol (EG), is an

attractive process both economically and environmentally. 1,2-PDO is used for polyester resins, pharmaceuticals, antifreeze, cosmetics, and tobacco humectants. 1,3-PDO is a highly valued chemical that is mainly used in specialty polyester fibers, films, and coatings¹²⁻¹³. The various products that may be obtained from glycerol hydrogenolysis are shown in Figure A.1.



Figure A.1: Possible products of glycerol hydrogenolysis.

Different groups have studied Ru catalysts yielding different conversions and selectivities towards 1,2-PDO¹⁴⁻⁴⁵. In one of the earliest works on glycerol hydrogenolysis over ruthenium catalysts, Montassier et al. observed that monometallic Ru catalyst preferentially breaks the C-C bond instead of the C-O bond, which results in degradation products¹⁵. These authors utilized Ru/SiO₂ catalysts and found that methane was the main product, along with ethane and propane, as expected products of complete hydrogenation. Special attention should be given to acidic promoters for Ru/C, such as Amberlyst 15, that reach a conversion of about 79% with a selectivity of 75% to 1,2-PD at 393 K, a relatively mild temperature¹⁴. Feng et al. used a 5% Ru/Al₂O₃ to catalyze glycerol hydrogenolysis at

453 K and a hydrogen pressure of 5 MPa to obtain a conversion of 34.3 % with a 47.3 % selectivity to 1,2-PDO¹⁶. As it will be shown, these reported values are similar to those found with the home made catalysts used in this work. Lee and Moon have also used 5% Ru/Al₂O₃, and obtained a 45.6 % conversion with a selectivity of 59.2 % for 1,2-PDO¹⁷.

When investigating the activity of Cu catalysts, Montassier et al. observed that for the Cu-Raney catalyst, under a hydrogen pressure of 3 MPa and a temperature of 513 K, 86% of the product selectivity was 1,2-PDO¹⁵. Other authors have also tested copper for this reaction and obtained good selectivity for 1,2-PDO¹⁸⁻²¹.

The use of Ru alloys with other noble metals has been also investigated. Maris and Davis have investigated glycerol hydrogenolysis over Pt and Ru catalysts²², as well as the effect of bimetallic Pt-Ru and Au-Ru catalysts²³, and saw levels of conversions near 100% in alkali reaction environments, with varying selectivities. The authors have seen that nonetheless Pt is less active than Ru to activate C-C bonds. Roy et al. used commercial Pt/Al₂O₃ and Ru/Al₂O₃ and showed that hydrogenolysis occurred in the absence of H₂, by generating hydrogen via heterolytic cleavage of H₂O on Pt sites²⁴.

When studying the effect of Cu in Ru catalysts, Jiang et al. have worked with Ru-Cu clay supported catalysts for glycerol hydrogenolysis and have seen that a decrease in Ru/Cu ratio causes a drop in conversion with a relative increase in 1,2-PD selectivity²⁵. Rouco et al. used Ru-Cu and Ru-Ag catalysts supported on silica for the hydrogenolysis of ethane and both catalysts displayed a decrease in activity when compared to the monometallic ruthenium, since Cu and Ag have a lower activity in breaking C-C bonds²⁶. Guo et al. utilized Cu/Al₂O₃ under mild conditions (493 K and H₂ pressure of 1.5 MPa), yielding a 49.6 % conversion with a selectivity of 96.8 % for 1,2-PDO²⁷. Vasiliadou and co-authors performed the glycerol hydrogenolysis reaction under 513 K and 8 MPa, finding a conversion of 40.5 % with a 60.5 % selectivity using Ru/ZrO₂, and a conversion of 26.7 % with a 39.7 % selectivity when using Ru/Al₂O₃²⁸.

In a work with similar interests as this one, Liu et al. investigated the influence of the support on Ru-Cu catalysts²⁹. The catalysts used by those authors had a Ru/Cu atomic ratio of about 10/1 and were supported on TiO₂, SiO₂, ZrO₂, Al₂O₃, HY and NaY. They noted that Ru-Cu/ZrO₂ had the best performance. Since they observed no 1,3-PDO while acetol was present in the products, the authors have proposed a mechanism that differs from the one envisaged by Montassier et al.: dehydration of glycerol occurs first, generating acetol, then hydrogenation takes place. The difference between the two reaction pathways, (Figure A.2a) from Montassier et al.¹⁵ and (Figure A.2b) from Liu et al.²⁹, can be seen in Figure A.2. Balaraju et al. have summarized the question stating that solvent medium and catalyst acidity have a great influence on reaction mechanism, thus pathway (a) is due to alkali catalysts while acetol in pathway (b) is due to acidic catalysts³⁰.

Shimizu et al. have investigated the interaction of hydrogen with bimetallic Ru-Cu surfaces and have inferred that, given the non-homogeneous alloy, three different kinds of regions for Cu can be identified on the surface of the system, wherein even small percentages of Cu on the surface (>4%) may cause H_2 adsorption to drop drastically, compared to Ru adsorption³¹. These authors have also considered that the immiscibility of the metals, and thus lack of an ensemble effect, allows the presence of various possible new adsorption sites for H_2 , e.g. kink and terrace sites. Sinfelt et al. studied the Ru-Cu

system and found the same trend on the hydrogen chemisorption capacity that the authors above cited³².



Figure A.2: Proposed mechanisms for 1,2-PDO production through glycerol hydrogenolysis over Ru-Cu catalysts; (a) Montassier et al.¹⁵; (b) Liu et al.²⁹.

However, in our previous work, we investigated the interaction of bimetallic Ru-Cu/TiO₂ surfaces by XPS and the binding energies of both Ru and Cu in the bimetallic catalysts were similar compared to the monometallic catalysts and revealed no clear trend with composition, suggesting that electron transfer between the two metals in the bimetallic catalysts was minimal³³. We had also observed that when Cu was mixed with Ru in the given proportion, there was a slight decrease in H/Ru, likely the result of Cu deposition onto the Ru surface of 1:1 to 1:5 Ru/Cu. In agreement to the fact that hydrogen chemisorption is not enhanced by increasing the Cu weight loading, Rouco et al. found that as the nominal Cu/Ru molar ratio of a Cu-Ru/SiO₂ catalyst was increased from 0 to 0.667, the H/Ru ratio determined by H₂ chemisorption remained approximately constant²⁶.

More recently, Cu-based glycerol hydrogenolysis studies have been especially focused on the use of Y-zeolite supported catalysts³⁴, on the effect of preparation methods in the catalyst activity of Cu/SiO₂³⁵, on Cu-Cr bimetallic sites with high Cu⁰/Cu⁺ ratios³⁶,

and glycerol hydrogenolysis over Pt in tandem with methanol aqueous phase reforming (APR) over Cu:Zn:Al bulk catalysts³⁷. On the other hand, Ru/TiO₂³⁸⁻³⁹, and Ru/zeolite systems⁴⁰⁻⁴¹ have been trending as proposed heterogeneous catalysts towards glycerol hydrogenolysis.

The present work has the objectives of describing the preparation, characterization, and evaluation of the performance of supported Ru-Cu bimetallic catalysts, which favor the production of 1,2-propanediol, 1,3-propanediol and ethylene glycol from glycerol hydrogenolysis. Moreover, turnover frequencies (TOF) are calculated for the Ru-Cu systems, which are scarce in the literature. Bimetallic catalysts are known to produce distinct selectivities in some reactions, especially hydrogenolysis [32]. The following characterization techniques were employed: temperature programmed reduction (TPR), X-ray diffraction (XRD), textural analysis by N₂ adsorption, H₂ chemisorption, transmission electronic microscopy (TEM), and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). To evaluate the influence of reaction parameters, such as hydrogen pressure, temperature, and initial concentration of glycerol, catalytic tests were performed in a high-pressure reactor.

A.2 Experimental

A.2.1 Catalysts preparation

The catalysts prepared for this work were monometallic Ru, monometallic Cu, and Ru-Cu, each supported on Al₂O₃ or ZrO₂. The loading of each metal was 2.5 wt%. The catalysts were prepared by successive incipient wetness impregnations of Ru and Cu. The

catalysts were prepared using $Ru(NO)(NO_3)_3$.H₂O (Aldrich), and $Cu(NO_3)_2$.3H₂O (Sigma Aldrich) as the precursor salts. Al₂O₃ was obtained by calcination of boehmite (Catapal) in air for 3 h at 823 K with heating rate of 5 K min⁻¹. After metal impregnation, the supported catalysts were dried at 393 K for 12h followed by calcination in air at 623 K for 4h with heating rate of 2.5 K min⁻¹.

A.2.2 Catalyst characterization

Surface areas and pore volumes were determined by N_2 physisorption at 77 K, using the BET analysis method employing an ASAP 2010 Micromeritics analyzer. Prior to the measurements, the samples were degassed at 523 K for 6 h.

The X-Ray Diffraction (XRD) patterns were performed in a Rigaku (Miniflex II) diffractometer with a CuK α (1.540 Å) radiation.

The temperature programmed reduction (TPR) experiments were carried out on a sample (0.5 g) that was dried under flow of He (30 mL min⁻¹) for 30 min at 423 K and then cooled to room temperature. Temperature programmed reduction was performed under 30 mL min⁻¹ of flowing H₂ while the samples were heated to 723 K at 10 K min⁻¹. The measurements were carried out in a multipurpose unit coupled to a quadrupole mass spectrometer (Pfeiffer Vacuum, Prisma TM).

Hydrogen chemisorption was performed in a Micromeritics ASAP 2020 automated adsorption analyzer. The samples were reduced at 573 K under flowing H_2 for 60 min, and then outgassed under vacuum at 573 K for 60 min. After this, the catalysts were cooled to 308 K and evacuated again for 60 min followed by analysis at 308 K. The total amount of

 H_2 adsorbed was calculated by extrapolating the hydrogen uptake to zero pressure, assuming a stoichiometry H/Ru_{surf} equal to unity.

CO chemisorption measurements were carried out in the same multipurpose unit used for TPR. The catalyst samples (ca. 50 mg) were pretreated under a flow of He (30 mL min⁻¹) for 30 min at 423 K and then cooled to room temperature. The activation step took place at 573 K under a flow of 5% H₂/Ar (30 mL min⁻¹) for 1 h, followed by flushing under a flow of He for 30 min at 573 K and cooling to 300 K. CO uptake was measured by injecting a number of CO pulses and the exposed Ru was calculated assuming a CO/Ru molar ratio of 1/1.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of adsorbed carbon monoxide was performed with a Bruker VERTEX 70 spectrometer with a high-temperature DRIFTS cell (Harrick, HVC-DRP-4), fitted with ZnSe windows, and a diffuse reflectance accessory with Praying Mantis geometry. Spectra were acquired at a resolution of 4 cm⁻¹, typically averaging 256 scans. The samples were initially pretreated with a He flow (30 mL min⁻¹) for 30 min at 423 K. Then, the temperature was raised to 573 K in pure H₂ flow (30 mL min⁻¹) for 1h. After the reduction, the sample was flushed in He flow for 30 min, followed by cooling at 303 K. CO adsorption was then performed under CO/He flow (30 mL min⁻¹) for 30 min at 303 K, followed by flushing of the sample for 15 min with He and before recording spectra. To determine the thermal desorption of the adsorbents, the sample temperature was increased stepwise in continuous He flow. Images of the catalysts were obtained by transmission electron microscopy (TEM) (FEI Titan) at 300 kV and a Gatan 794 Multi-scan Camera to analyze metal particle size. At least 300

particles were analyzed from each sample. The samples were prepared by suspending the catalysts in ethanol, and agitating them in an ultrasonic bath for 10 min; then drops of the suspension were applied to a Cu mesh grid.

A.2.3 Catalytic Tests

Glycerol hydrogenolysis reactions were carried out in a 300 mL stainless steel batch reactor (Parr 4848). The reaction conditions were: temperature of 453 K, initial hydrogen pressure of 2.5 MPa, mass of catalyst of 1.2 g and 100 mL of glycerol (20 wt% in water). The reaction time was 24 hours with stirring of 500 rpm.

Prior to the reaction, the catalyst was reduced at 573 K for 1h, in a separate unit, under a flow of pure H_2 (30 mL min⁻¹), followed by oxidation under a flow of 5% O₂/He (15 mL min⁻¹) for 15 min at 273 K.

The reaction sequence was as follows: load the reactor with the glycerol solution and the appropriate amount of catalyst, purge with a flow of N₂ (30 mL min⁻¹) for 5 min, and treat in flowing H₂ (30 mL min⁻¹) at ambient temperature for 1 h in the reaction vessel. The temperature and H₂ pressure were then increased to the desired values under constant stirring. The batch reaction proceeded for a 24 h period. After 24 h, the system was cooled to ambient temperature and liquid and gaseous samples were collected. The liquid phase products were analyzed and identified by a GC-MS (Shimadzu, GCMS-QP2010S) equipped with a 95% polyethylene glycol (PEG) wax RTX column. The gas phase was sampled and analyzed in a 490 Micro-GC (Agilent) equipped with three columns: M5A 9 (H₂, O₂, N₂, CH₄ and CO), 5CB (PoraPLOT U CO₂ and C₂H₆) and PPU(CP-Sil 5CB – Hydrocarbons). CH₄ was obtained as a gas product in an amount less than 1%. The identified products were: 1,2-PDO, 1,3-PDO and 1-propanol as products of the hydrogenolysis reaction and ethylene glycol (EG), ethanol, methanol and methane as degradation products of glycerol. Product and reactant concentrations were calculated using measured response factors.

A.3 Results and discussion

A.3.1 Catalysts Characterization

The surface areas and pore volumes of the supports and prepared catalysts are shown in Table A.1. As it can be seen, for Al₂O₃ supported catalysts, there was an 8% decrease in area by the addition of either 2.5 wt% Ru or 2.5 wt% Ru and 2.5 wt% Cu. On the other hand, for ZrO₂ supported catalysts, there was the same decrease in area when adding Ru metal, but adding both Ru and Cu had a stronger effect on the support surface area.

Figure A.3 shows the X-ray diffractograms, in which five characteristic peaks for Ru and RuO_x are observed. The broadest peaks are assigned to Ru⁰. There are no detected Cu peaks in the bimetallic catalyst. The Scherrer formula provides an inverse proportionality relationship between crystal size and XRD peak width, in a way that broader peaks are related to smaller particles⁴². If this relation holds for monometallic Ru/Al₂O₃ and bimetallic Ru-Cu/Al₂O₃, the average particle sizes lie in the range of 3.5-5 nm. Particle size analysis by TEM showed a slightly larger particle size, but they were on the same order of magnitude. On the other hand, peaks corresponding to RuO_x were not detected on the ZrO₂ supported catalyst probably because peaks from the crystalline zirconia support mask any contributions from RuO_x.

Catalyst	Surface area (m²/gcat)	Pore volume (cm ³ /gcat)	H2 µmol/g _{cat}	Fraction of Ru Exposed (H/Ru)	TEM particle diameter (nm)	Surface average diameter (nm)
γ-Al ₂ O ₃	193	0.80	-	-	-	-
Ru/γ - Al_2O_3	178	0.42	77.0	0.623	6.3 ± 3.1	9.8
Ru-Cu/γ-Al ₂ O ₃	177	0.39	69.2	0.560	10.7 ± 6.1	14.8
ZrO_2	19	0.08	-	-	-	-
Ru/ZrO ₂	18	0.08	4.3	0.035	8.1 ± 3.6	13.7
Ru-Cu/ZrO ₂	9	0.07	11.9	0.096	10.2 ± 9.1	12.8

Table A.1. BET surface area, pore volume, metal dispersion results by H chemisorption, and transmission electron microscopy (TEM) particle analysis for Ru supported catalysts.

The TPR profiles for the catalysts used in this work are displayed in Figure A.4, and the results of the analyses are shown in Table A.2. The reduction efficiency was calculated as the amount of H₂ consumed over the theoretical amount required to reduce RuO_3 and CuO. According to the literature, precursor salts seem to have a great effect on reduction efficiency. Many values for RuO₂ reduction temperature can be found, especially for catalysts prepared with RuCl₃ as a precursor salt⁴³⁻³⁸. Koopman et al.⁴³ have reported that for Ru/SiO₂, reduction of RuO₂ takes place between 450 K and 478 K, and McNicol and Short⁴⁴ have reported that there is a single peak at 443 K for bulk unsupported RuO₂. According to Hurst et al., the reduction of RuNO(NO₃)_x may present different profiles, depending on the reduction of NO and the x number of NO₃ groups⁴⁵. Mazzieri et al. reported that ruthenium oxide reduction takes place at 470 K, while a shoulder may also be seen, representing the reduction of the oxichloride for $RuCl_3^{46}$. Using $Ru(acac)_3$ as the precursor, Bianchi has reported that reduction of RuO₃ to RuO₂ occurs with a small peak at 393 K, and that RuO₂ to Ru⁰ takes place at 483 K with a much larger peak⁴⁷. In this work, monometallic Ru/Al₂O₃ showed a small peak of reduction at about 438 K, a shoulder
at about 473 K, and a broader and larger peak at 558 K. From these peaks it could be inferred that the first peak represents higher oxidation states, the shoulder would be RuO₃ and the last peak RuO₂. This agrees partially with the range of reduction (450-525 K) reported by Lee and Moon¹⁷. The TPR profiles for monometallic Ru/ZrO₂ and Ru/Al₂O₃ obtained in this work differ notably from each other, which might be caused by different interactions of the precursor salt and the supports. The Ru/ZrO₂ catalyst shows only one broad peak that begins at 421 K and ends at about 450 K, whereas Ru/Al₂O₃ has a very broad reduction peak around 558 K.

Table A.2. Results of TPR analysis for Ru based catalysts.

Cotolyct	Catalyst mass	H ₂ consumption	Reduction		
Catalyst	(mg)	(mmol)	efficiency* (%)		
Ru/γ - Al_2O_3	503.6	0.337	91.3		
Ru-Cu/γ-Al ₂ O ₃	484.0	0.525	97.3		
Ru/ZrO ₂	509.8	0.314	84.1		
Ru-Cu/ZrO ₂	422.3	0.482	100.0		

*Calculated taking RuO₃ and CuO as the species subject to total reduction.

When investigating TPR profiles for Ru-Cu/Al₂O₃, Galvagno et al. noted that using RuCl₃ as the precursor salt, the addition of Cu generated a shoulder, which shifted the Ru reduction peak closer to the lower Cu reduction temperature⁴⁸. This was attributed to the interactions between support and the metallic salts. This is corroborated by the present work, in which it has been seen that the Cu addition favored reduction of Ru at lower temperature for Ru-Cu/Al₂O₃. The bimetallic Ru-Cu/ZrO₂ profile displayed a broader range for reduction, which is related to the addition of Cu. Since cluster formation is expected for Ru and Cu mixtures, instead of homogeneous alloys⁴²⁻⁴⁹, it can be inferred that the shifts in reduction temperature may be caused by inter-phase hydrogen adsorption, which favors Cu reduction. Another evidence of this is the observed simultaneous

reduction of Cu and Ru species for the bimetallic $Ru-Cu/Al_2O_3$ and $Ru-Cu/ZrO_2$, indicating some interaction between the two metals.

Carbon monoxide DRIFTS results are shown in Figure A.5. Cu/Al₂O₃ displayed a sharp peak at 2100 cm⁻¹, Ru/Al₂O₃ showed a very weak peak at 2064 cm⁻¹, and the bimetallic Ru-Cu/Al₂O₃ showed both distinct 2100 cm⁻¹ and a broad peak at 2009 cm⁻¹. Gottschalk et al. reported the same value of 2064 cm⁻¹ for Ru/Al₂O₃⁴¹. Brown and Gonzalez have assigned the 2080 cm⁻¹ frequency to a Ru–CO σ -bond, as the main peak for Ru/SiO₂ supported catalysts⁵¹, while Unland⁵² found that Ru has weak peaks at 2009 cm⁻¹ and 2070 cm⁻¹, and Kim et al.⁵³ have associated the CO chemisorption on Cu/SiO₂ at 2125 cm⁻¹. Therefore, it can be said that while Ru had a poor performance in CO adsorption, Cu, on the other hand, acted as promoter of adsorption in the Ru-Cu/Al₂O₃ bimetallic catalyst, with a blue-shift of about 25 cm⁻¹. For the ZrO₂ supported catalysts, although Ru/ZrO₂ displayed a strong peak at 2070 cm⁻¹, in accordance with Unland⁵², the addition of Cu blueshifted the peak to about 2060 cm⁻¹, decreasing its amplitude. The Cu⁺-CO species is known to occur at 2158 cm⁻¹ for zeolites⁵⁴, and the obtained value of 2100 cm⁻¹ for the intense absorbance band of Cu/Al₂O₃ could be attributed to Cu⁺. The formation of Cu²⁺ sites seems to be disfavored.



Figure A.3: X-ray diffractograms for (a) Al_2O_3 , Ru/Al_2O_3 , $Ru-Cu/Al_2O_3$; (b) ZrO_2 , Ru/ZrO_2 , $Ru-Cu/ZrO_2$.



Figure A.4: Temperature Programmed Reduction of (a) Ru/γ -Al₂O₃, Ru-Cu/ γ -Al₂O₃ and Cu/ γ -Al₂O₃; (b) Ru/ZrO₂, Ru-CuZrO₂.



Figure A.5: Carbon monoxide DRIFTS of (a) Ru/γ -Al₂O₃, Cu/γ -Al₂O₃ and Ru-Cu/\gamma-Al₂O₃ catalysts; (b) Ru/ZrO_2 and Ru-Cu/ZrO₂ catalysts.

TEM micrographs of the catalysts and their respective size distributions are presented in Figure A.6. As it can be seen, ruthenium particles were larger for Ru/ZrO_2

than for Ru/Al₂O₃. Additionally the dimensions of bimetallic Ru-Cu/Al₂O₃ particles were somewhat more frequently larger, in the range of 8-10 nm.





Figure A.6: TEM micrographs and the corresponding particle size distribution of (a) Ru/Al₂O₃; (b) Ru/ZrO₂; (c) Ru-Cu/Al₂O₃; (d) Ru-Cu/ZrO₂.

A.3.2 Hydrogenolysis of Glycerol

Glycerol conversion and the selectivity of Ru based catalysts used for the hydrogenolysis reaction are presented in Table A.3. Selectivity was calculated as the ratio of product moles produced over the total moles of glycerol converted. The different sets of

catalysts showed various performances towards the hydrogenolysis reaction. For all of the evaluated catalysts, the products identified were: 1,2-PDO, EG, 1,3-PDO, 1-propanol, ethanol and methanol. Methane, CO and CO₂ were also found in the gas phase.

Selectivity %			
Others ^c			
20.2			
4.4			
2.6			
-			

Table A.3: Conversions and selectivity of the catalysts used in the present work.

*Reaction conditions: 20 wt% gly solution; T: 453K; H₂ Pressure: 2.5 MPa; 500 rpm, 24h

^aBased on total liquid phase products.

 $^b\mbox{Based}$ on total liquid phase products normalized to the H_2 chemisorption capacity of the fresh catalyst

^cOthers: 1-propanol, 2-propanol, ethanol, methanol, and acetol

Acetol was detected as a final product in these reactions at very low concentrations. However, Vasiliadou et al. found a significant amount of acetol after 5 h of reaction²⁸. Their experiment was performed under severe conditions, using 8MPa of hydrogen pressure, at 513K and pure glycerol. The presence of acetol in every experiment was interpreted by those authors as a possible intermediate product of the dehydration/hydrogenation mechanism, which finally yields 1,2-PDO after a hydrogenation step, in agreement with the literature⁵⁵⁻⁵⁸. The absence of acetol in the present work may be possibly explained by the longer duration of the reaction (24 h).

The main identified product in all catalytic reactions studied was 1,2-PDO, except for Ru/Al₂O₃, which presented about equal quantities of 1,2-PDO and EG. The best conversion was obtained with monometallic Ru/Al₂O₃ catalyst, with a varying selectivity to possible products. When compared with Ru/ZrO₂, it could be inferred that the extra activity of alumina is due to acidity, since glycerol protonation may favor OH cleavage. The 1,3-PDO selectivity was not pronounced in practically any of the tested catalysts. The Ru-Cu/ZrO₂ catalyst presented the highest selectivity towards 1,2-PDO (100%) followed by Ru-Cu/Al₂O₃ (\approx 92%). Under 503 K and 8 MPa, a previous study showed that a 3%Ru-1%Cu/Al₂O₃ catalyst converted 100% of glycerol with a selectivity of 85% for 1,2-PDO²⁵. Table A.4 shows a comparison between the tested catalysts in this work and those described in the literature. By comparing the results, although better conversion values have been reported, the selectivity obtained by this work, 91.9 %, had not been yet reported for that reaction temperature (473 K).

Catalysts	Conversion (%)	Selectivity (%) 1,2-PDO	References	
Ru/γ - $Al_2O_3^a$	45.6	59.2	17	
Ru/γ - $Al_2O_3^b$	69.0	37.9	28	
Ru/γ - $Al_2O_3^c$	32.8	41.7	This work	
Ru/ZrO_2^b	40.5	60.5	28	
Ru/ZrO2 ^c	30.1	69.8	This work	
Ru/C ^d	49.2	74	52	
3%Ru-0.19%Cu/Al ₂ O ₃ ^e	68.0	37.0	29	
3% Ru-1%Cu/ γ -Al ₂ O ₃ ^f	100	85	25	
3%Ru-0.19%Cu/ZrO ₂ ^e	100	84	29	
2.5% Ru- 2.5% Cu/ γ -Al ₂ O ₃ ^c	45.0	94	This work	

Table A.4: Comparison of conversion and selectivity for the hydrogenolysis reaction of various Ru based catalysts.

^aHydrogen pressure 2.5MPa at 453 K; ^b Hydrogen pressure 8MPa at 513 K; ^c Hydrogen pressure 2.5MPa at 473 K; ^d Hydrogen pressure 8MPa at 403 K; ^e 60 %wt. glycerol aqueous solution, 0.5 mL; reaction temperature, 180°C; Hydrogen pressure, 10.0 MPa; ^f Hydrogen pressure 8MPa at 503 K.

The effect of temperature on catalyst selectivity for Ru-Cu/Al₂O₃ was also investigated. Although a more complex model for glycerol hydrogenolysis may be suitable, available kinetic data for glycerol conversion agree with a first order reaction. Table A.5 shows the apparent specific velocity constants, k_{app} , the initial rate of consumption of glycerol per volume, $R_{V,0}$, the initial rate of consumption per catalyst gram, $R_{m,0}$, the initial turnover frequency, TOF₀, for each of the given temperatures. The squared sample correlation coefficients, r^2 , for all temperatures were between 0.992 and 0.996. Although considerable difficulties are encountered in calculating the actual TOF, in this work the TOF was normalized by H₂ chemisorption⁵⁹. Upon comparing the specific velocities, and using least squares methodology, the apparent barrier energy can be shown to be 63.5 kJ/mol, which agrees with the value reported by Lahr and Shanks (62 kJ/mol) for glycerol hydrogenolysis over ruthenium⁶⁰. It should be noted that the turnover frequencies for Ru/ZrO₂ catalysts are remarkably greater than for the other catalysts, due to the smaller number of H₂ adsorption sites that offer relatively the same apparent specific reaction velocity. The conversion range and kinetic fitting used in this article is in agreement with a prior work done by our group with Ru-Cu/TiO₂ catalysts, regarding TOF calculations, based on first order kinetics³³.

All catalysts tested in the hydrogenolysis reaction behaved as described in the corresponding literature. In the present work, Ru-Cu/ZrO₂ displayed the best 1,2-PDO yield, with 100% selectivity at low conversion, as it can be seen in Table A.3, with slightly less conversion compared to monometallic ruthenium, corroborating Liu et al.²⁹. In the present work, monometallic Cu/Al₂O₃ catalyst did not show activity for the glycerol

hydrogenolysis reaction²⁷. The discrepancy from the conversion obtained in this work with

other referenced values is attributed to the larger glycerol to catalyst mass ratio²⁵⁻²⁹.

Table A.5: Temperature dependence of conversion, apparent specific velocities, reaction rates and turnover frequencies of glycerol hydrogenolysis reaction over Ru-Cu/Al₂O₃ considering first order kinetics.

Temp. Conv. (K) (%) ^a	Conv	Conv. $k_{app}/10^{-6}$ (%) ^a (s ⁻¹) ^b	$R_{V,0}/10^{-6}$ (mol.L ⁻¹ .s ⁻¹) ^c	$R_{m,0}/10^{-6}$ (mol.g _{cat} ⁻¹ .s ⁻¹) ^d	TOF ₀ /10 ⁻⁶ · (s ⁻¹) ^e	Selectivity (%)			
	(%) ^a					1,2- PDO	EG	1,3- PDO	Others ^f
453	20.6	2.41	5.498	0.436	0.780	91.9	3.7	-	4.4
473	45.0	6.96	15.882	1.261	2.254	94.0	6.0	-	-
493	53.6	9.37	21.388	1.697	3.036	76.8	6.2	0.6	15.8

Hydrogen pressure 2.5MPa, 500 rpm, 1.2 g catalyst, 20% wt. glycerol solution.^a Based on total liquid phase products; ^b k_{app} : apparent first order rate constants; ^c $R_{V,0}$: initial rate of consumption of glycerol per liquid volume; ^d $R_{m,0}$ initial rate of consumption of glycerol per liquid volume; ^d $R_{m,0}$ initial rate of consumption of glycerol per catalyst gram; ^e Based on total liquid phase products normalized to the H₂ chemisorption capacity of the fresh catalyst; ^f others: 1-propanol, 2-propanol, ethanol, methanol, acetol.

The mass ratio of glycerol/catalyst used in the present work (16.7 $g_{Glycerol}/g_{cat}$) is

much larger than the ones reported by Jiang et al. (about 5.4 $g_{Giycerol}/g_{cat})^{25}$, and by Liu et al. (about 6.0 $g_{Giycerol}/g_{cat})^{29}$. According to ref.²⁵ an optimal atomic ratio of Ru/Cu is 3:1, whereas for ref.²⁹ optimal ratio was found at 10:1. Since the conditions used in the present work differ greatly from the conditions used in refs.^{25,29}, regarding glycerol/catalyst mass ratios, it does not seem adequate to offer accurate comparisons. It is, however, safe to say that Ru-Cu exhibits interesting catalytic behavior in a range from 10:1 to 10:16 of Ru/Cu atomic ratios for both ZrO₂ and Al₂O₃ as supports, from which the best activities are found in the lower Cu content region, since hydrogen chemisorption is not favored by Cu in the active sites. Besides this, somewhat contradictory to refs.^{25,29}, the greater Ru/Cu fraction used in this work does not seem to have any negative effect towards 1,2-PDO production,

since 100% selectivity was obtained for Ru-Cu/ZrO₂, as seen in Table A.3, which could point to other influencing factors in the reaction, such as solvent action.

The low specific rate per gram of catalyst tested for the reaction can be related to the low dispersion of the ruthenium particles, as showed in Table A.1. The incipient wetness impregnation method used for the preparation of the catalysts did not produce a high particle dispersion. Balaraju et al. evaluated the influence of preparation methods and the metal content in TiO₂ supported ruthenium catalysts, and observed that when the catalyst was prepared by the incipient wetness impregnation the glycerol conversion (31 %) was lower than when the method was precipitation $(44 \%)^{13}$. These authors implied that the low conversion presented by the catalysts prepared by the conventional method is related to the low metal particle dispersion over the supporting material.

Recycling experiments were performed for the monometallic catalysts, the results of which can be seen in Table A.6. Both Ru/Al₂O₃ and Ru/ZrO₂ catalysts showed a drop on the order of ~ 5% in activity, in the first recycle. The Ru/ZrO₂ catalyst showed the more dramatic drop in activity after the second recycle (about 58% from the first recycle). Comparatively, Al₂O₃ appears to offer a more stable support for the catalyst, exhibiting a 20 % drop from the first recycle.

By interpretation of the obtained characterization and glycerol hydrogenolysis activity data for the materials, it is possible to propose a model for the bimetallic catalysts' surfaces, as follows. The first step is to consider that Ru and Cu are highly immiscible, and given its atomic size and mass, Cu atoms are more likely to form particles on top of the Ru structure. The second step is to consider that both metals present different space group structures. While reduced Ru forms hexagonal close packed (hcp) crystals (P6₃/mmc), Cu forms face-centered cubic (fcc) crystals (Fm-3m). For fcc crystals, the basal plane (110) is the one with least atomic density, while the (111) plane presents the closest packing, from which hexagonal surfaces should be expected as the most stable cleavage configuration. Therefore, it is reasonable to suspect that the Cu atoms would organize themselves in hexagonal layers over already assembled bulk hcp Ru nano-particles. The third step is to consider the actual diffractogram of Ru-Cu/Al₂O₃, in which Cu-related peaks are absent, but Ru-related peaks are prominent. The influence of Cu coverage over Ru in hydrogenolysis activity is also a function of the reduction activation temperature prior to the reaction⁶¹. All reactions of this work were undertaken using a reduction temperature of 573 K, around the expected temperature range indicative of Cu mobility for multilayer deposition onto Ru, but far below temperatures of intensive sintering (>780 K). With this in mind, since Ru-Cu homogeneous alloy formation is unlikely^{59,61}, given the immiscibility of both metals, multi-layer deposition of Cu occurs, but not to the extent as to cover entirely the Ru surface at the reduction temperature of 573 K, or to separate entirely Cu clusters from the Ru particles.

This is evidence for considering Ru as the bulk particle phase, with thin layers of Cu on top of it. The bimetallic structure would thus be prone to anisotropy, with parts of the Ru crystal available for coordination or chemisorption-like phenomena, while the Cu sites would also display enhanced activity, from Cu⁺ sites. The monometallic Ru catalyst particles have an average diameter of 6 nm, and the bimetallic Ru-Cu catalyst particles

have an average diameter of about 11 nm, from which the increased length would be due

to the outer Cu cluster layers.

Carbon Selectivity (%) TOF/10⁻⁶ Conversion Cycle Catalyst Balance 1.2-1,3- $(s^{-1})^{b}$ EG $(\%)^{a}$ Others^c PDO PDO (%)1 0.8990 Ru/Al_2O_3 32.8 84 42 43 2 13 0.8575 2 Ru/Al_2O_3 30.8 91 51 37 5 8 7 3 0.7214 49 34 10 Ru/Al_2O_3 24.8 94 1 Ru/ZrO_2 30.1 89 7.4044 70 28 0 2 2 2 7 Ru/ZrO_2 28.7 90 7.1345 65 26 3 Ru/ZrO_2 12.0 100 3.3276 59 34 0 7

Table A.6: Recycle experiments with $2.5\%\,Ru/Al_2O_3$ and $2.5\%\,Ru/ZrO_2$ catalysts for glycerol hydrogenolysis

*Reaction conditions: 20 wt% gly solution; T: 453K; H₂ Pressure: 2.5 MPa; 500 rpm, 24h. The spent catalyst was recovered by filtration with a 0.45μ m pore membrane, washed with distilled, deionized water and dried at 393 K before recycle. ^aBased on total liquid phase products. ^bBased on total liquid phase products normalized to the H₂ chemisorption capacity of the fresh catalyst. ^cOthers: 1-propanol, 2-propanol, ethanol, methanol, and acetol

Finally, the effect these geometric factors have on the electron band structure for the bimetallic particle should also be considered. Both Ru and Cu are late transition metals, which is enough to envisage that electronic interactions between metallic particles and molecules will happen through sp and d bands and molecular orbitals of the adsorbate. While Cu has a completely filled, narrow d band, very near the Fermi level, Ru atoms have open shell 4d electrons, and therefore a broader d band in respect to the density of states. Thus, formation of small Cu clusters on the surface of Ru structures would create an asymmetric d band distribution along the bimetallic particle. As seen from the obtained activity data, Cu has the ability to direct selectivity towards the formation of 1,2-PDO in glycerol hydrogenolysis, avoiding further C-C bond breaking. This points to the fact that the band distribution is such that it enables back donation to C-O molecular orbitals upon adsorption, after which the C-C orbitals can not be further filled by the modified Ru d band, but rather a hydrogenation of the adsorbed C atom takes place.

A.4 Conclusion

The use of ruthenium-copper bimetallic catalysts in glycerol hydrogenolysis presents a viable alternative for 1,2-PDO production. There is considerable agreement between the literature and the results obtained in the present work, which shows the highest selectivity for 1,2-PDO by usage of Ru-Cu/ZrO₂ catalyst. The turnover frequency for the Ru-Cu/ZrO₂ is greater than for the Al₂O₃ bimetallic catalyst. An optimum proportion of Ru/Cu is situated in the region of low Cu content for best relation conversion/selectivity towards 1,2-PDO, and it appears that a convenient atomic ratio is 10:1. However selective Ru-Cu/ZrO₂ is, it should be noted that Al₂O₃ is a much more stable support for glycerol hydrogenolysis.

References for Appendix A

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Appendix B: Summary of Other Published Works

Ide, M. S.; Falcone, D. D.; Davis, R. J. "On the deactivation of supported platinum catalysts for selective oxidation of alcohols." *J. Catal.* **2014**, *133*, 295-305.

Abstract:

The oxidation of a variety of terminal alcohols with O₂ in liquid water at 343 K over Pt supported on C, BN, SiO₂, TiO₂, and Al₂O₃ was explored to determine the origin of catalyst deactivation. The sintering of Pt nanoparticles and dissolution of Pt did not contribute significantly to the observed deactivation. A decrease in TOF for 1,6-hexanediol oxidation after the exposure of Pt/C to dioxygen was easily reversed by reduction with the alcohol substrate, indicating that over-oxidation of Pt was not the mode of deactivation. Strongly adsorbed CO on Pt was observed by ATR-IR spectroscopy after contacting the catalysts with alcohols, but the CO was easily removed by oxidation with dissolved O₂. Results from thermogravimetric analysis and regeneration studies indicate a strongly adsorbed species other than CO and product acid deactivated the catalysts.

Tolborg, S.; Katerinopoulou, A.; Falcone, D. D.; Sádaba, I.; Osmundsen, C. M.; Davis, R. J.; Taarning, E.; Fristrup, P.; Holm, M. S. "Incorporation of Tin affects Crystallization, Morphology, and Crystal Composition of Sn-Beta." *J. Mat. Chem. A.* **2014**, *2*, 20252-20262.

Abstract:

The crystallization of Sn-Beta in fluoride medium is greatly influenced by the amount and type of tin source present in the synthesis gel. By varying the amount of tin in the form of tin (IV) chloride pentahydrate, the time required for crystallization was studied. It was found that tin not only drastically affects the time required for crystallization, but also that the presence of tin changes the morphology of the formed Sn-Beta crystals. For low amounts of tin (Si/Sn = 400) crystallization occurs within four days and the Sn-Beta crystals are capped bipyramidal in shape, whereas for high amounts of tin (Si/Sn = 100) it takes about sixty days to reach full crystallinity and the resulting crystals are highly truncated, almost plate-like in shape. Using SEM-WDS to investigate the tin distribution along transverse sections of the Sn-Beta crystals, a gradient distribution of tin was found in all cases. It was observed that the tin density in the outer parts of the Sn-Beta crystals is roughly twice as high as in the tin depleted core of the crystals. Sn-Beta was found to obtain its maximum catalytic activity for the conversion of dihydroxyacetone to methyl lactate close to the minimum time required for obtaining full crystallinity. At excessive crystallization times, the catalytic activity decreased, presumably due to Ostwald ripening.

Xie, J.; Falcone, D. D.; Davis, R. J. "Restructuring of supported PtSn bimetallic catalysts during aqueous phase oxidation of 1,6-hexanediol." *J. Catal.* **2015**, *332*, 38-50

Abstract:

A series of carbon-supported bimetallic PtSn catalysts having various Pt/Sn molar ratios was prepared and tested in the oxidation of 1,6-hexanediol with 1 MPa dioxygen at 343 K in aqueous solvent. The PtSn/C catalysts, which were initially reduced with sodium borohydride, did not produce Pt–Sn alloy particles. Instead, the catalysts were composed of SnOx moieties that were well-dispersed on the surfaces of the carbon support and the Pt nanoparticles. Subsequent treatment in H₂ at 673 K induced Pt–Sn alloy formation. Whereas addition of SnO_x to the Pt nanoparticles promoted the initial 1,6-hexanediol oxidation rate by 39%, the formation of Pt–Sn alloy particles decreased the initial rate. Under 1,6-hexanediol oxidation conditions, however, the Pt–Sn alloy phase separated, leading to the recovery of the catalytic activity. No significant change of product distribution was observed on bimetallic PtSn catalysts, regardless of the composition and structure.

Appendix C: Sample HPLC Chromatographs



Figure C.1: High performance liquid chromatograph for a typical glycerol hydrogenolysis reaction described in Chapters 2, 3, and 5. The analysis was conducted with an Alliance high performance liquid chromatograph (Waters e2695) equipped with a refractive index detector (Waters 2414) and an Aminex ion exclusion column (Bio-Rad, HPX-87H) operating at 318 K with a 0.5 M H_2SO_4 mobile phase.



Figure C.2: High performance liquid chromatograph for a glycerol hydrogenolysis reaction performed with N_2 in the reactor headspace at 8% conversion.