

BIMETALLIC PHOSPHIDE CATALYSTS FOR BIOMASS UPGRADING
REACTIONS

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Abstract

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The growing efforts in renewable energy development from biomass sources motivate the need of new catalytic material discovery. In particular, the depolymerization of long chain aromatics in biomass feed results in a variety of functional groups (predominantly oxygenated) that poses a challenge in terms of the quality of the biomass feed and the resilience of the required catalysts. Multifunctional catalysts that can transform a variety of functionalities simultaneously and can also withstand the operating conditions are needed. Metal phosphide catalysts have high potential for biomass upgrading due to their thermal stability and the nature of their active sites (i.e., acidic, reduced metal). Further catalytic enhancements are often observed with the incorporation of second metal to form bimetallic phosphides. However, a deeper understanding of the catalytic enhancement through bimetallic phosphides is still lacking.

This thesis focuses on the synthesis and detailed characterizations of various bimetallic phosphides as well as their catalytic evaluation for hydrodeoxygenation and hydrogenation reactions of oxygenated biomass compounds. Extensive studies on the oxidation state of Mo-based bimetallic phosphides $MMoP$ ($M = Fe, Co, Ni$) with x-ray photoelectron spectroscopy and x-ray absorption near edge spectroscopy show the relative oxidation of (i.e., $Mo^{\delta+}$) is highly dependent on the charge transfer between the atoms in $MMoP$ and most likely is the site for the interaction between the lone pair oxygen in phenol and the catalyst surface. Other bimetallic phosphides such as $RuMoP$ are found to be active for low temperature hydrogenation reactions ($<125^{\circ}C$) for various functionalized aromatics. Kinetic evaluations on monometallic and bimetallic Ru and Mo phosphides for furfural hydrogenation provide evidence for catalytic enhancement in bimetallic phosphides with a Ru:Mo:P ratio of 1:1:1 as the optimum composition for selective aldehyde conversion to alcohol. Lastly, bimetallic $NiMoP$ and $RuMoP$ are evaluated for a more complicated molecule such as cinnamaldehyde with conjugated C=C and C=O bond. $NiMoP$ shows favorable selectivity to the hydrogenation of thermodynamically favored C=C bond. Meanwhile, bimetallic $RuMoP$ favors the hydrogenation of C=O bond due to its surface electronics in combination with surface crowding by the products that prevents C=C adsorption. The studies in thesis emphasize the importance of finding the optimum surface electronics through material modifications in bimetallic phosphides for biomass upgrading reactions.

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CHAPTER 1

GENERAL INTRODUCTION AND PROJECT MOTIVATION[†]

1.1 Biomass feed diversity

Lignocellulosic biomass is a renewable carbon source that can meet global energy and chemical needs.¹⁻³ Commonly found in plants and crops, lignocellulosic biomass is composed of cellulose (40-50%), hemicellulose (25-35%), and lignin (18-35%).⁴ Cellulose and hemicellulose are constructed of polysaccharides wherein cellulose contains only glucose and hemicellulose contains cross-linked sugar monomers other than glucose (Figure 1.1a-b).⁴⁻⁵ The depolymerization of cellulose yields C6 sugars, while hemicellulose yields C5 sugars. Meanwhile, lignin contains of cross-linked phenolic polymeric chains. The representation of the three main monomers of lignin is presented in Figure 1 as coniferyl alcohol, *p*-coumaryl alcohol, and sinapyl alcohol Figure (1.1c). The C6 aromatic-rich content of lignin makes it a promising renewable fuel source.

Although the lignocellulosic biomass constituents are rich in C-source, the contents of the constituents depend largely on the types of the plant sources

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(Table 1.1). This feed diversity causes a continually changing and unpredictable compositions in biomass feed. As a result, the characteristic and product qualities of the resulting chemicals derived from the biomass stream are heavily influenced by the source of the biomass feed. Therefore, the subsequent upgrading step must be able to withstand this feed diversity.

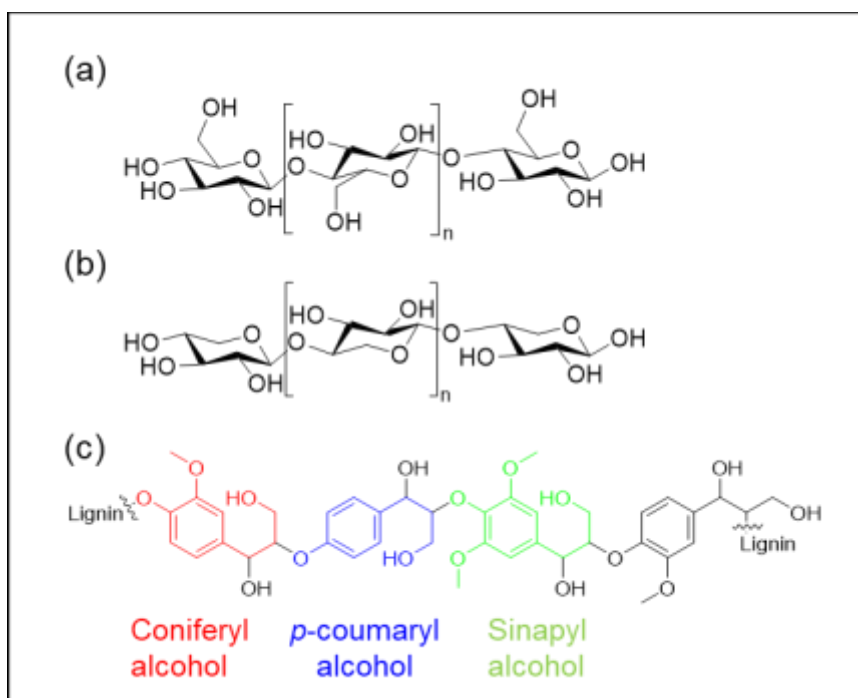


Figure 1.1. The representation of (a) cellulose, (b) hemicellulose, and (c) lignin chemical structures. [Adapted from ref.⁶]

Regardless, several pretreatment techniques are implemented to break the polymeric chain in cellulose, hemicellulose, and lignin to smaller chain molecules to facilitate less complicated upgrading.

TABLE 1.1.
LIGNOCELULLOSIC BIOMASS CONTENT IN PLANTS⁷

Sources	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	40-55	24-40	18-25
Softwood stems	45-50	25-35	25-35
Switch grass	45	31.4	12-20
Corn stover	35-40	17-35	7-18
Wheat straw	30	50	15
Newspaper	40-55	25-40	18-30

1.1.1 Processing techniques

Multiple strategies have been investigated to depolymerize biomass into platform molecules that can be directly converted to useful fuels and chemicals. The two main conversion processes are (1) thermochemical methods and (2) hydrolysis (Figure 1.2).^{3, 8}

1.1.1.1 Thermochemical methods

Thermochemical pretreatment involves a controlled oxygen and thermal environment to promote chemical transformation in biomass. Thermochemical methods include gasification, liquefaction, and pyrolysis.

The gasification process converts biomass into gas products and solid product (i.e., char). The gas products include synthesis gas (i.e., CO and H₂) that can be further processed by either Fischer-Tropsch chemistry to yield alkanes or directly converted to methanol. Some light hydrocarbons like ethane or propane have also been collected after the process. This is an endothermic process that

is carried out with air and steam. Although this process yields valuable gasses, many potential carbon derivatives are lost in the process due to the combustion process taking place.⁹

Pyrolysis process involves heating up biomass in the absence of air or oxygen. The main concept of pyrolysis is using high heat (450-600°C) to break chemical bonds to form molecules with lower molecular weight.⁹ The heating rate of the pyrolysis process influences the ratio between liquid and solid products where faster heating rate is desired to reduce solid products (i.e. fast pyrolysis).¹⁰ The liquefaction process produces bio-oil through heating at lower temperature than pyrolysis (250-450°C) at high pressure (50-200 atm) in the presence of catalyst, solvent, and reducing gas (H₂ or CO).³ This method produces a bio-oil with lower oxygen content, and thus a higher heating value.^{3, 11} Even so, the fast pyrolysis method is preferred since it does not require the use of costly H₂.

Regardless of the method, biomass depolymerization results in a mixture of many (>400) functionalized components such as carboxylic acids, esters, ketones, alcohols, furans, aldehydes, sugars, and phenolics.^{3, 12-13} As mentioned above, the compositions of the final bio-oil depends greatly on the biomass feed sources. Additionally, the thermochemical conditions such as water content, storage time, heating time, temperature, and air content also affect the final content of the bio-oil creating a diversity of chemicals in the final product.¹³

1.1.1.2 Hydrolysis

In the thermochemical method, the biomass feed is processed as a whole creating a mixture of organic compounds. On the other hand, the hydrolysis of lignocellulosic biomass separates sugars (cellulose and hemicellulose) in an aqueous environment from the lignin portion of the mixture.¹⁴ The sugars can then be either fermented to form bioethanol or dehydrated to form furanics or higher molecular weight alkanes. However, the recalcitrant nature of lignin inhibits the fermentation process. Therefore, the lignin portion is separated during the pretreatment of the biomass. In both the thermochemical and hydrolysis method, there are various organic compounds that need to be upgraded further to a higher value-added chemicals and fuels.

1.1.2 Biomass feed upgrading reactions

Many upgrading reactions have been employed for biomass oxygenates and derivatives such as hydrogenation, hydrodeoxygenation (HDO), coupling, dehydration, and etc. However, this thesis will only focus mainly on HDO and selective hydrogenation reaction.

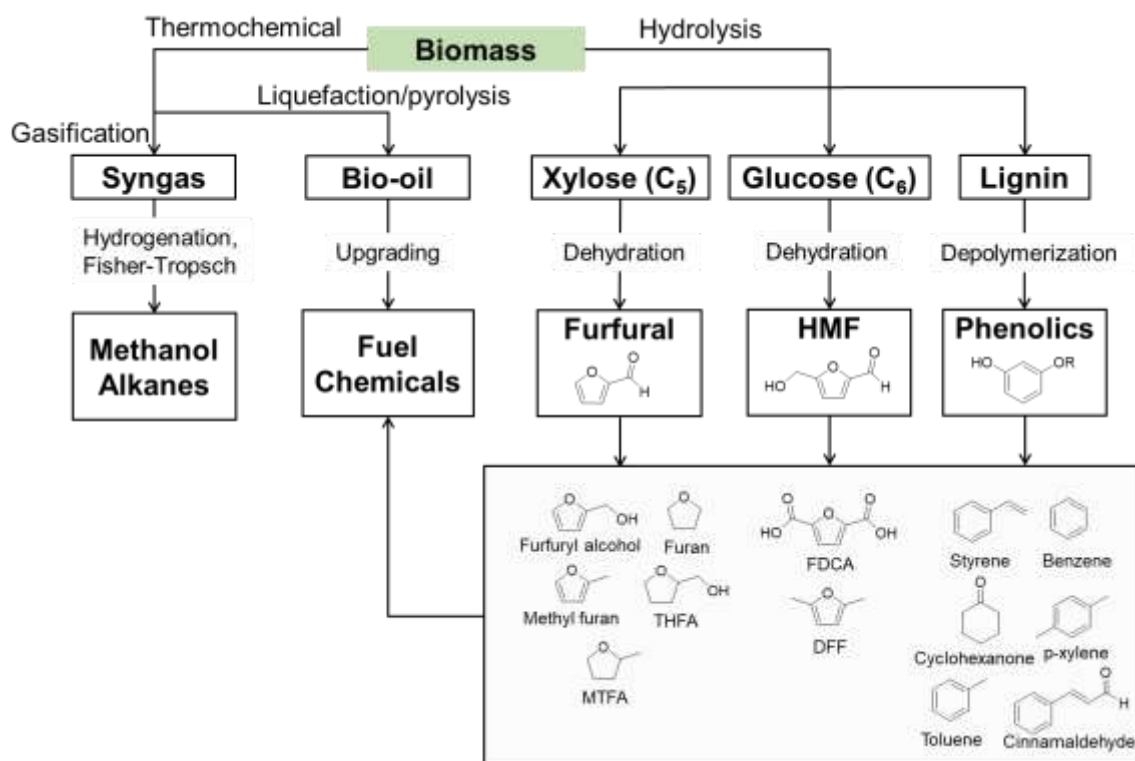


Figure 1.2. Biomass upgrading routes and examples of possible chemicals derived after upgrading. [Adapted and modified from ref.^{8, 15-16}]

1.1.2.1 Removal of oxygenates

Biofuel is targeted as a replacement for the current petroleum stream to achieve neutral carbon balance. However, the highly oxygenated mixtures of bio-oil have to be upgraded further by employing a process that is able to deoxygenate and thus stabilize the bio-oil to meet the petroleum requirements.¹⁷ One common method of accomplishing this is through a hydrodeoxygenation (HDO) reaction to cleave the C-O aromatic bonds. In HDO reactions, high pressure H_2 is used to cleave C-O bonds to form water, alcohols, and hydrocarbons.¹⁷ The stability of bio-oils is increased after the HDO process due to lower oxygen content.

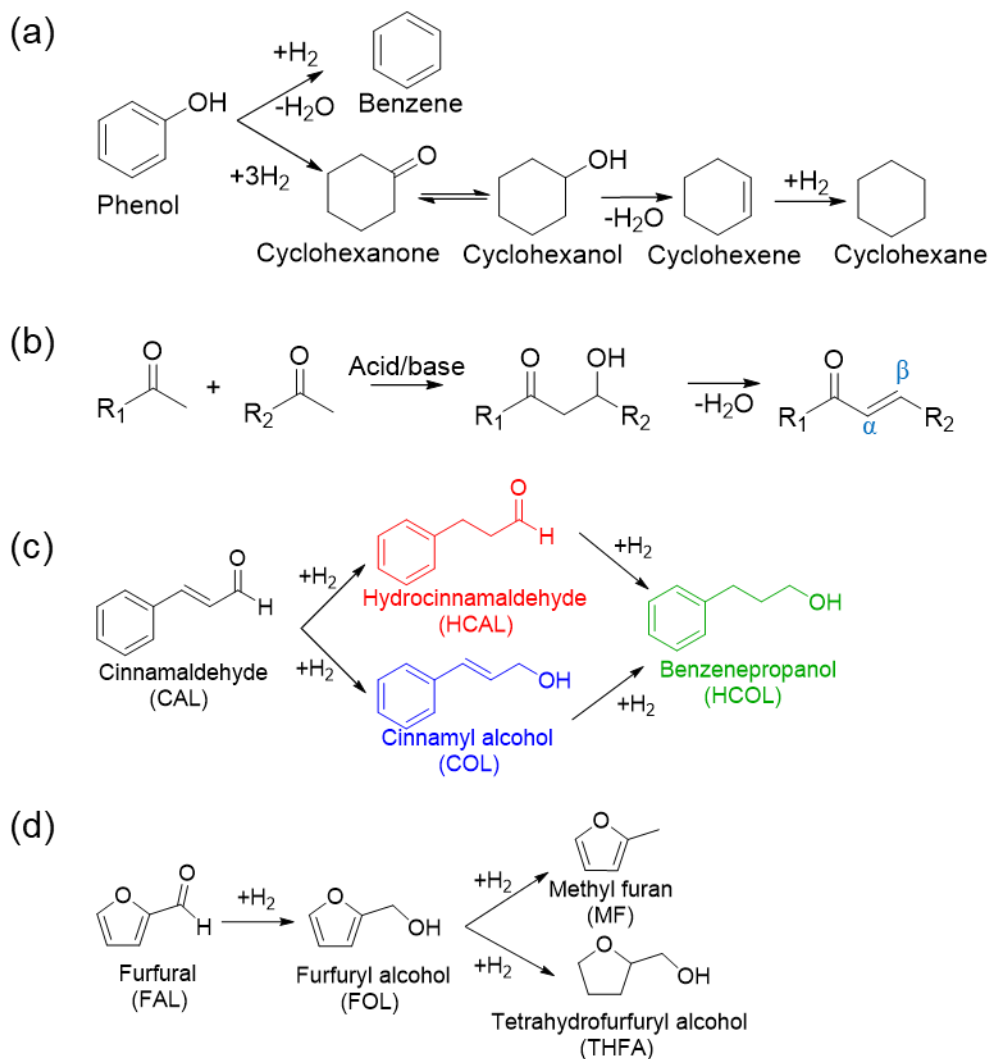


Figure 1.3. Reaction pathway for (a) phenol hydrodeoxygenation, (b) aldol condensation, (c) cinnamaldehyde hydrogenation, and (d) furfural hydrogenation

Model compounds such as phenol are often used in HDO studies to demonstrate the C-O_{aromatic} cleavage ability of the catalysts. Ideally, the deoxygenation occurs through the cleavage of C-O_{aromatic} bond while preserving the aromaticity of the ring resulting in better H₂ economy. This reaction pathway is commonly referred to as direct deoxygenation (DDO) depicted in Figure 1.3a. However, the C-O_{aromatic} bond breaking energy is 468 kJ/mol, 83 kJ/mol higher

than a C-O_{aliphatic} bond dissociation energy.¹⁷ Often, the deoxygenation occurs after the aromatic ring is saturated. This pathway is called the hydrogenation pathway (HYD). Experimental and computational studies indicated that surface-O interaction is pivotal in driving the C-O bond cleavage.¹⁸⁻²¹ Therefore, an understanding in surface-O interaction is desired to design a material that can directly cleave the C-O_{aromatic} bond.

1.1.2.2 Selective hydrogenation of α,β -unsaturated carbonyl

Aldol condensation is a challenging reaction in biomass upgrading that involves C-C coupling of carbonyl compounds forming an aldol adducts that dehydrates into an α,β -unsaturated carbonyl (Figure 1.3b).²² The selective hydrogenation of α,β -unsaturated carbonyl is complicated due to the competition between C=O and C=C bond reduction (Figure 1.3c). The C=O bond hydrogenation is challenging since thermodynamics favor hydrogenation of the C=C bond with ΔH_{rxn} (C=O) of -66 kJ/mol and ΔH_{rxn} (C=C) of -134 kJ/mol. α,β -unsaturated aldehydes such as crotonaldehyde and cinnamaldehyde are often used as model compounds to demonstrate the selective reaction. Selective C=O bond hydrogenation have been demonstrated in many systems including ones using aluminum isopropoxide and metal hydride.²³⁻²⁴ However, the disposal of the resulting metal salts is problematic. Therefore, solid catalysts that can selectively hydrogenate C=O bond is needed. Many catalyst design factors such as particle size, support effect, shape selectivity, solvent, and alloying are used

as strategy to tune the selectivity.²⁵⁻³² Specific catalyst reviews that have been used for this reaction is included in Chapter X.

1.1.2.3 Hydrogenation of other oxygenated compounds

The hydrolysis of hemicellulose in acidic media results in monosaccharides primarily consisting of xylose (C5).³³ The dehydration of xylose results in furfural formation.³³ There are around 80 derivative molecules that can be derived from furfural.³⁴ However, furfural itself is highly unstable and reactive. Therefore, immediate upgrading of furfural is necessary.

The hydrogenation of the aldehyde group in furfural yields furfuryl alcohol that is used as a monomer for furan resin. Currently, roughly 60% of furfural is converted into furfuryl alcohol. The challenge is, however, other side reactions such as C-O bond cleavage forming methyl furan, decarbonylation forming furan, or ring hydrogenation forming tetrahydrofurfuryl alcohol could occur (Figure 1.3d). These side products are also of industrial significance. For example, methyl furan is used as an alternative fuel additives, while tetrahydrofurfuryl alcohol is used as a solvent or intermediate for other chemicals.^{23, 35-37} Although these derivative chemicals are of industrial significance, selective hydrogenation to produce one product is still desired to reduce separation.

Even though these products have value, selective catalysts are still desired to isolate one product. In this thesis, furfuryl alcohol is chosen as a target molecule due to its industrial value. The current catalyst, Cu-chromite, is environmentally undesirable and thus its disposal is problematic. Moreover, the

catalyst deactivates within two hours of time on stream. Hence, a new recyclable catalyst is needed for this process.

1.1.2.4 Other reactions

The upgrading of the diverse bio-oil involves many other reactions beyond what is covered in this thesis. Diels-Alder cycloaddition has been proposed as a potential route to produce selective aromatic monomers. The Diels-Alder reaction occurs through the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of diene and dienophile. The addition results in cycloadduct formation that can dehydrate into new unsaturated bonds. The choice of dienes usually involves (but not limited to) furanic-type compounds since they contain conjugated dienes. Meanwhile, a wide variety of unsaturated dienophiles can be chosen depending on the desired end functionality. In the biomass context, this reaction is used to synthesize functionalized phenyl groups (C6+) from shorter carbon chains. This C-C coupling method yields aromatics with high carbon efficiency.

Although many of the upgrading reactions target deoxygenation, the oxidation reaction can also be advantageous. Furandicarboxylic acid (FDCA) along with ethylene glycol (EG) are precursors to the bio-based polymer polyethylene 2,5-furandicarboxylate (PEF). FDCA is obtained from the oxidation of the aldehyde and alcohol functionals of hydroxymethylfurfural (HMF) to carboxylic acids. HMF is obtained from the hydrolysis of cellulose followed by a dehydration step. This upgrading reaction is challenging due to the multiple

intermediate products that can be obtained during oxidation. Routes such as electrochemistry, biocatalysis, and solid catalysts (i.e., metal oxides) have been explored.³⁸

1.2 Phosphide catalysts

The complex reactive systems described above require the use of multifunctional catalysts, which I define here as a catalyst with multiple distinct sites that are capable of handling the high diversity of reactants in the initial feedstock such as in biomass feed.³⁹ Transition metal phosphides are among the best candidates because they constitute a broad group of multifunctional materials that possess high acidity, reduced metal character, and high thermal stability.

1.2.1 Physical properties

Transition metal phosphides are stable materials formed by alloying most transition metals in the periodic table with phosphorus.⁴⁰ They were first discovered in the 17th century by Andreas Marggraf by the addition of small amount of white phosphorus to a metal with heat.⁴¹⁻⁴² The physical properties of phosphides resemble the hardness and strength of ceramics and they exhibit high conductivity similar to metals, which results in high thermal stability with a melting point range of 827-1527°C.⁴³ Interestingly, metal phosphides are also found in meteorites as (Fe,Ni)₂P or better known as barringerite and allabogdanite as well as in (Fe,Ni)₃P composition.⁴⁴⁻⁴⁵ Other Fe and Ni compositions can also be found terrestrially such as (Fe, Ni)₂P and (Fe, Ni)₁P.⁴⁶

The magnetic properties of phosphides can be altered to exhibit different behaviors based on their composition.⁴⁷ For example, cobalt phosphide, Co_2P , is paramagnetic, but the addition of iron to form $\text{Co}_x\text{Fe}_{2-x}\text{P}$ changes the material to ferromagnetic.⁴⁸ In terms of their structures, metal rich phosphides adapt diverse crystal structures such as hexagonal, cubic, and orthorhombic (Figure 1.4).⁴³

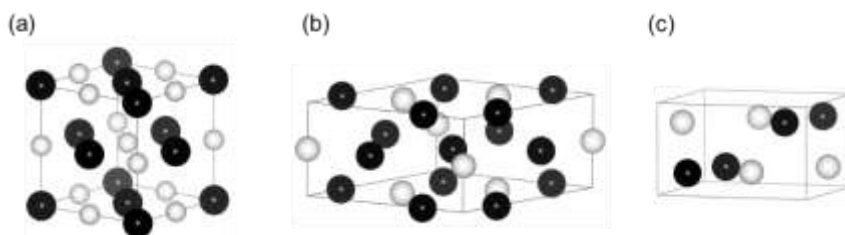


Figure 1.4. Example of phosphides crystal structures for (a) cubic, (b) hexagonal, and (c) orthorhombic unit cells. The metal is represented in black and phosphorus is represented in white.

1.2.2 Proposed active sites

The Lewis and Brønsted acid sites have been proposed as active sites in metal phosphides. The Lewis acidity most likely exists from the electron deficient site as a result of charge transfer between the metal(s) and P atom as observed in x-ray photoelectron spectroscopy (XPS) and x-ray absorption near edge spectroscopy (XANES). The oxidation state of the elements in metal phosphides are near 0. However, XPS and XANES are able to resolve subtle shift in the binding energy and absorption energy respectively. A majority of literature reports shifts in the metal(s) to the higher energy, while the energy of the P atom shifts to the lower energy. This indicates partial positive charge in the metals ($\text{M}^{\delta+}$) and partial negative charge in the P atom ($\text{P}^{\delta-}$). Note that some metals can

also carry a partially negative charge such as one in Ru-based bimetallic phosphide ($\text{Ru}^{\delta-}$). Nevertheless, the electron deficient $\text{M}^{\delta+}$ is the most plausible source of Lewis acidity in metal phosphides. Meanwhile, Brønsted acidity in metal phosphides could arise from incomplete reduction of the precursor to form P-OH species on the surface.⁴⁹ The acidity can be characterized with pyridine adsorption under infrared spectroscopy.⁵⁰⁻⁵¹ Pyridine coordinatively bonds to the Lewis acid site with several IR features at $\sim 1620\text{ cm}^{-1}$ and $\sim 1420\text{ cm}^{-1}$ for ν_{8a} and ν_{19b} mode respectively.⁵² Brønsted acid protonates the N lone pairs of pyridine to yield features at $\sim 1550\text{ cm}^{-1}$ for ν_{19b} mode. The ν_{19a} vibration mode, however, shows a feature at $\sim 1480\text{ cm}^{-1}$ for both Lewis and Brønsted acid interactions. Although the presence of both Lewis and Brønsted acidity have been reported in metal phosphide such as $\text{Ni}_2\text{P}/\text{SiO}_2$, the Lewis acid features are dominant.⁵³⁻⁵⁴

Other active sites that have been proposed are the tetrahedral M(1) and square pyramidal M(2) sites formed when the metal (M) sites are coordinated with four and five P atoms respectively. These sites can be distinguished and quantified using Mössbauer spectroscopy⁵⁵⁻⁵⁸. The M(1) and M(2) sites are distinguishable by the size of split in the spectra. The M(1) sites show single line or double line with small splitting, while the M(2) site shows a doublet with large splitting.⁵⁶ Extended x-ray absorption fine structure (EXAFS) can also be used to determine the presence of M(1) and M(2) sites. For example, the Ni-P distance in Ni(1) and Ni(2) in Ni_2P are 2.23 Å and 2.43 Å respectively. By assuming Ni(1) or Ni(2) coordination, the EXAFS data can be fitted to a theoretical Ni(1) or Ni(2)

model to obtain a Ni-P coordination numbers to confirm the presence of Ni(1) or Ni(2) sites.

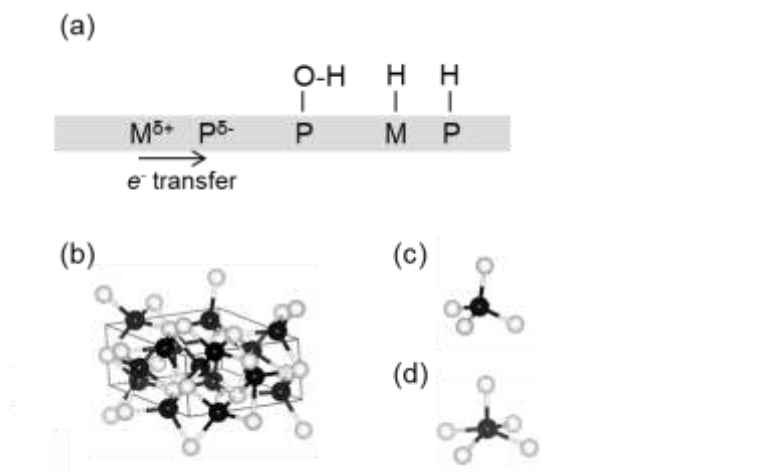


Figure 1.5. (a) The proposed active sites on metal phosphides, (b) unit cell of hexagonal metal phosphides, (c) tetrahedral sites, and (d) square pyramidal sites.

Although these active sites mostly focused on the metal sites, the P site has recently been proposed as active as a H-adsorption site through density functional theory (DFT) calculations.⁵⁹ Adsorption top site is energetically favorable in a P-terminated surface in MoP(001) although adsorption on the Mo-terminated hollow sites are still more favorable.⁵⁹ Further, the any loss in P would create a defect that can expose the Mo atom for H-adsorption.⁵⁹ These active sites are illustrated schematically in Figure 1.5.

1.3 Synthesis methods of metal phosphides

The synthesis methods of phosphides can be classified based on the treatment of the precursors. In the temperature programmed reduction (TPR)

method, the pre-mixed precursors are reduced under a H_2 environment to form the phosphides. The resulting materials are highly pyrophoric and are often passivated with dilute O_2 immediately after synthesis. This method is versatile and does not require an O_2 -free environment for storage of the synthesized material. Of course, each phosphide will have a different O_2 stability and will need to be assessed accordingly. Moreover, the starting materials are generally inexpensive forms of metal nitrates or chlorides. However, this method requires high synthesis temperatures ($> 500\text{ }^{\circ}C$) that sinters the particles and decreases the surface areas. The second synthesis method involves the decomposition of metal complexes (Figure 1.7). As its name implies, the precursors or intermediates are usually amorphous metal complexes. The final step of the synthesis includes annealing at much lower temperatures ($< 350\text{ }^{\circ}C$) than the TPR method to yield the metal phosphides. The final products are often in suspension and are separated by filtration/washing. An advantage of this method is the formation of nanoparticles with controllable shapes and particle sizes.

1.3.1 Temperature programmed reduction

Due to its versatility, TPR is one of the most common synthesis methods in heterogeneous catalysis, in which the metal precursors (salt, oxides) and a source of phosphorus (phosphate, phosphorous acid) are subjected to a flow of H_2 at high temperatures. In the phosphate method, ammonium phosphate dibasic is used as the phosphorus source, while in the phosphite method

phosphorous acid is used. Since the oxidation state in phosphorous acid is +3, lower than the phosphorus oxidation state in phosphate precursor (+5), the P-O bond is weaker and thus the reduction temperature needed to form the phosphide is lower than the phosphate method (Figure 1.6).⁶⁰

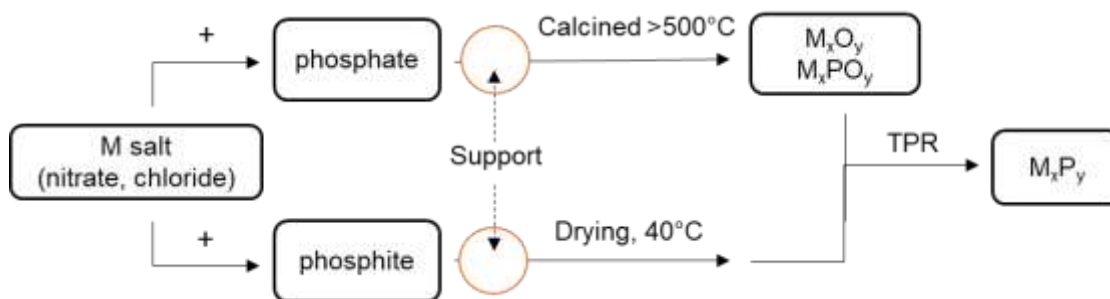


Figure 1.6. Synthesis pathway through TPR method

The TPR processes involve dissociation of H_2 in the early reduction step of the metals, which continues to spillover to the phosphorus precursor (phosphate) to form reduced phosphorus or phosphine (PH_3).⁶⁰ The resulting phosphorus-containing intermediates react with the metal to form a solid solution of the metal phosphide. This mechanism is supported by a series of studies that tracked the formation of Ni_2P on SiO_2 from the calcined precursor of $Ni(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_2HPO_4$.⁶¹ The x-ray diffraction (XRD) data showed that at reduction temperature of $400^\circ C$ and below, only NiO is present. As the temperature is increased, a metallic Ni peak is observed followed by $Ni_{12}P_5$ formation and finally Ni_2P at $600^\circ C$ and above.⁶¹ When the same study is performed on MoP/SiO_2 , MoP features are observed at lower reduction temperatures of $\sim 500^\circ C$.⁶¹

TPR can be used to synthesize either unsupported or supported metal phosphides. Phosphides synthesized using the phosphate method have larger particle sizes due to sintering that occurs with high synthesis temperatures (400°C-1000°C).⁶⁰ This is a drawback because high surface areas are often desired to improve the gram-based reaction rates of the resulting catalysts. Over the years, efforts to improve the surface area of unsupported phosphide catalysts have been made by the addition of organic materials such as polymer surfactant polyethylene glycol *tert*-octylphenyl ether (Triton X-114) and ethylene glycol that yielded unsupported Ni₂P at 500°C under this method with a S_{BET} of 130 m²/g.⁶² In addition, citric acid has also been investigated as an organic additive to increase the surface area of unsupported metal phosphides. The addition of citric acid with ratio of 2 to 1 with respect to the metal increases the S_{BET} of unsupported MoP from 8 m²/g to 136 m²/g.⁶³ The citric acid behaves as a structural promoter during calcination to prevent the agglomeration of particles during reduction, resulting in smaller particle sizes of 5-9 nm.⁶³

Many of the typical catalyst supports, such as SiO₂ and γ-Al₂O₃ can be used with metal phosphides. As reported by various researchers, phosphide synthesis on supported material requires an excess amount of the phosphorus source due to the possibility of strong interactions between the phosphorus precursor and the support.⁶⁴⁻⁶⁵ Moreover, it is also possible that PH₃ formed during the reduction step is evacuated in the flowing H₂ stream.⁶⁰ To study potential support effects, Ni₂P has been synthesized at different precursor ratios supported on SiO₂ and γ-Al₂O₃.⁶⁵ It was determined that γ-Al₂O₃ interacts strongly

with the phosphate precursor to yield AlPO_4 causing (1) the reduction temperature to be 200 °C higher compared to $\text{Ni}_2\text{P}/\text{SiO}_2$, which further increased the particle size and (2) higher P/Ni precursor ratios are required for the synthesis. Unfortunately, $\gamma\text{-Al}_2\text{O}_3$ is a commonly used support in the industry due to its durability. Therefore, supporting phosphides on $\gamma\text{-Al}_2\text{O}_3$ using this method is not advised unless the formation of AlPO_4 is desired.

The synthesis of bimetallic phosphides, such as NiMoP , using the TPR method is also feasible.^{61, 66} By comparing temperature-dependent diffraction patterns, the XRD crystalline intermediates of NiMoP is predominantly MoO_3 .⁶¹ Similar phenomena are observed in another bimetallic phosphides synthesis, FeMoP , through the analysis of each step of the synthesis with XRD and Raman.⁶⁷ In agreement with the work mentioned above on the synthesis of NiMoP , after the calcination step of the precursors, only MoO_3 and FePO_4 are observed in both XRD and Raman. The combination of SEM and EDS showed that FePO_4 envelopes the MoO_3 phase, and further thermal reduction yields FeMoP .⁶⁸

Another possible source of phosphorus in TPR is phosphorous acid, which forms a metal phosphite when mixed with the metal precursor.⁶⁰ In the synthesis of $\text{Ni}_2\text{P}/\text{SiO}_2$, the initial TPR peak occurs at 420°C, while the phosphate method shows the first reduction peak at 590°C, possibly due to weaker P-O bond in the phosphite precursor.^{60, 69} This results in higher S_{BET} of various monometallic phosphide catalyst (i.e. SiO_2 supported Ni_2P , CoP , WP , MoP , FeP) with the phosphite method.⁶⁹

Regardless of the precursor, transition metal phosphide synthesis via TPR results in highly active catalytic materials that are discussed later in this chapter. The disadvantage of this method is the required high reduction temperature, which results in sintering and reduces the surface area of the materials.

1.3.2 Metal organic decomposition

The most common nanoparticles synthesis is carried out through reaction of metal complexes with trioctylphosphine (TOP). Various monometallic and bimetallic phosphides nanoparticles have been synthesized through this widely-studied route to yield size-controlled and shape-controlled materials. The general procedure involves the reaction between the metal complexes (i.e. nickel acetylacetonate, iron pentacarbonyl) with TOP and oleylamine at $\sim 220^{\circ}\text{C}$ to yield amorphous materials followed by annealing at higher temperature (i.e. 350°C) for further crystallization and phosphidation of the materials (Figure 1.7). Oleylamine is the reducing agent that controls nucleation rate, while TOP stabilizes the nanoparticles to prevent aggregation of the particles.⁷⁰ Variation in the starting materials yields Ni_2P nanoparticles with tunable size between 2-30 nm.⁷⁰ The formation of hollow nanoparticles is the consequence of the Kirkendall effect, in which the different diffusion rates of the species (i.e. Ni and P) results in a hollow particle formation.⁷¹⁻⁷² In this case, the core diffusion of Ni outwards is faster than the diffusion of P inwards.⁷¹ The Kirkendall effect could, however, be avoided when the metal Ni nanoparticles intermediates are small enough ($\sim 5\text{ nm}$)⁷² or at high P/Ni ratios.⁷³ This method can also be used to synthesize Ni_{12}P_5 with a

variety of Ni:P ratio. The size of the hollow particle could also be controlled from 5-60 nm when the amount of triphenylphosphine (PPh_3) is varied to synthesize Ni_2P .⁷⁴ Other phosphides can also be synthesized with this method (FeP , Fe_2P , PtP_2 , Rh_2P , Au_2P_3 , and Pd_5P_2).^{72, 75}

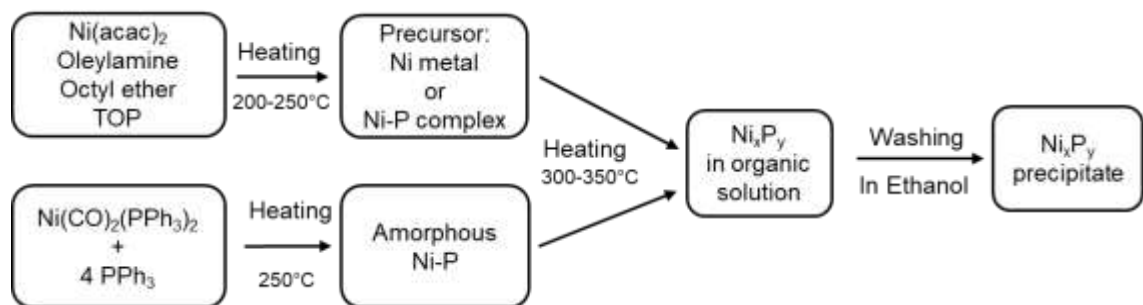


Figure 1.7. Synthesis pathway for metal complex decomposition.

Moreover, the same method can be used to synthesize bimetallic phosphides such as $\text{Fe}_x\text{Ni}_{2-x}\text{P}$, $\text{Ni}_x\text{Co}_{2-x}\text{P}$, and $\text{Fe}_x\text{Co}_{2-x}\text{P}$.⁷⁶ The synthesis initiates by the formation of amorphous Ni-P precursors using the method above followed by the addition of a Fe precursor (i.e. $\text{Fe}(\text{CO})_5$) continued with further heating to crystallize $\text{Fe}_x\text{Ni}_{2-x}\text{P}$. Based on Mössbauer spectroscopy, Fe occupies the tetrahedral sites for $x < 0.8$ due to electron transfer and populates square pyramidal sites at higher compositions.⁷⁶ Spherical particles are preferred at $x < 1.2$ and rod-shaped particles formed at higher Fe content.

To summarize, nanoparticle synthesis can be done through metal complex decomposition either starting from a metal precursor and TOP illustrated in the top route on Figure 1.7 or by a single-source precursor depicted in the bottom of Figure 1.7.

1.3.3 Hypophosphite precursor method

Another method uses hypophosphite as the phosphorus source and a metal oxide as the metal source. In the first reaction step, hypophosphite precursor is reduced to PH_3 at 300°C , which reduces the metal oxide precursor to form a metal phosphide, excess phosphorus, and water. Since phosphorus is always a product in the synthesis, generally this method requires an excess amount of hypophosphite. This method, however, requires a lower temperature than the TPR method due to the weaker M-O bonding compared to P-O, and thus less thermal energy is required. However, PH_3 is hazardous and thus the synthesis must be carried in a safe environment. Although the synthesis is performed at low temperatures, the resulting particle size from this synthesis method is fairly large ($\sim 3.2\ \mu\text{m}$) for Ni_2P , Cu_3P , MoP , and InP .⁷⁷⁻⁷⁸ Another similar method incorporates either gas phase PH_3 or dissolved PPh_3 in liquid directly into the metal and support to achieve high density active sites.⁷⁹⁻⁸⁰ Solvothermal methods have been employed to synthesize CoP , Co_2P , Cu_3P , and Ni_2P , which we refer the reader to the cited literature for more information.⁸¹⁻⁸³

1.4 Catalytic applications of metal phosphides

1.4.1 Heteroatom removal in petroleum feeds

Hydroprocessing is an integral part of the petroleum refining industry to dramatically reduce heteroatom content in transportation fuels to comply with strict environment requirements. Sulfur, for instance, exists in recalcitrant and sterically hindered dibenzothiophene (DBT), and its derivatives, which are

removed during HDS.⁸⁴⁻⁸⁵ Due to the bulky nature of the molecule, sulfur removal is quite challenging. In general, there are two reaction pathways that could proceed in HDS: direct desulfurization (DDS) and hydrogenation followed by desulfurization (HYD).^{84, 86-89} Figure 1.8 illustrates the reaction network for 4,6-dimethyl DBT (4,6-DMDBT). The DDS pathway yields 3,3'-dimethyl biphenyl (3,3'-DMBP) directly, while the hydrogenation pathway results in methylcyclohexanetoluene (MCHT) and dimethylbicyclohexane (DMBCH). The DDS pathway is often desired because it reduces the consumption of H₂, as all of the H₂ is used directly for C-S bond cleavage and H₂S production.

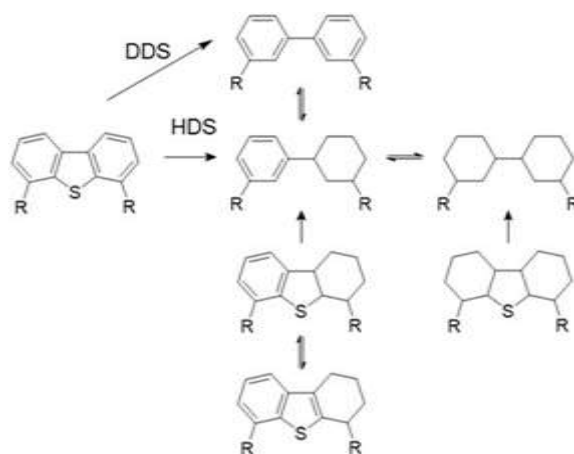


Figure 1.8. Reaction pathway in hydrodesulfurization.

Another important reaction in hydroprocessing is the more challenging HDN to remove compounds such as quinolines and porphyrins. In most cases, HDS catalysts have been evaluated for HDN reactions, as these two reactions ideally should proceed simultaneously. To avoid new capital investments required to implement new processes, novel “drop-in” materials have been explored to replace

alumina supported, sulfided NiMo and CoMo, which are currently used industrially. Metal phosphides (notably Ni₂P) outperform other classes of catalysts like sulfides and carbides because the charge transfer in Ni-P bond provides a “ligand effect” that favors dissociation of the reactant and H₂. Additionally, ensemble effects exist that lead to moderate bonding of the surface with products of the reactions. These effects prevent site poisoning from the strong bonding of S atoms.⁹⁰⁻⁹¹ Many review articles have covered this issue in detail,^{43, 60, 88, 92-93} and some of the notable findings are summarized below.

Nickel phosphides are the most studied metal phosphides for hydroprocessing. In fact, Ni₂P is the first phosphide to be used as a hydrogenation catalyst for benzonitrile.⁹⁴ Years after, other groups also investigated Ni₂P as a hydrogenation catalyst for butadiene.⁹⁵⁻⁹⁶ Over the years, numerous studies have reported the HDS and HDN activity of monometallic phosphide catalysts such as Ni-P, Fe-P, Co-P, MoP, WP, Rh-P, Ru-P, Pt-P, and Pd-P.⁹⁷⁻⁹⁸ Comparisons between the catalytic properties observed from each catalyst is not always possible due to the difference in synthesis and reaction conditions from different research groups. Some works have, however, compared the catalytic performance of several metal phosphides under the same conditions. Based on these studies, the activity for dibenzothiophene HDS and quinoline HDN increase in the following order: Ni₂P/SiO₂ > WP/SiO₂ > MoP/SiO₂ > CoP/SiO₂ > Fe₂P/SiO₂.⁸⁸

The active sites of phosphides are identified by correlating catalysis data with EXAFS of Ni₂P synthesized on various supports including MCM-41, low surface area L90 SiO₂ (SiO₂-L) and high surface area EH5 SiO₂ (SiO₂-H).⁵⁸ For the

HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT), the surface area, dispersion, and hydrogenation (HYD) selectivity of the catalyst decreases in the order of $\text{Ni}_2\text{P}/\text{MCM-41} > \text{Ni}_2\text{P}/\text{SiO}_2\text{-H} > \text{Ni}_2\text{P}/\text{SiO}_2\text{-L}$. The direct desulfurization (DDS) selectivity is higher on the catalyst with lower dispersion and larger particle size. Both tetrahedral and square pyramidal sites (Figure 1.5c-d) are present in all catalysts, but a higher number of Ni(1) is present in the catalyst favors the DDS reaction pathway. Therefore, the Ni(1) site has been directly associated with the DDS pathway, while the Ni(2) site are correlated with the HYD pathway.⁵⁸ This result has been further supported by another study where Fe was incorporated in $\text{Ni}_2\text{P}/\text{SiO}_2$.⁵⁷ This incorporation of Fe decreases the HDS activity of the material, but increases the selectivity towards the DDS product.⁵⁷ Although density functional theory calculations indicate no preferential site occupation between Ni(1) and Ni(2) sites, the incorporation of Fe decreases the number of Ni(2), which explains the increase in DDS selectivity.⁹⁹

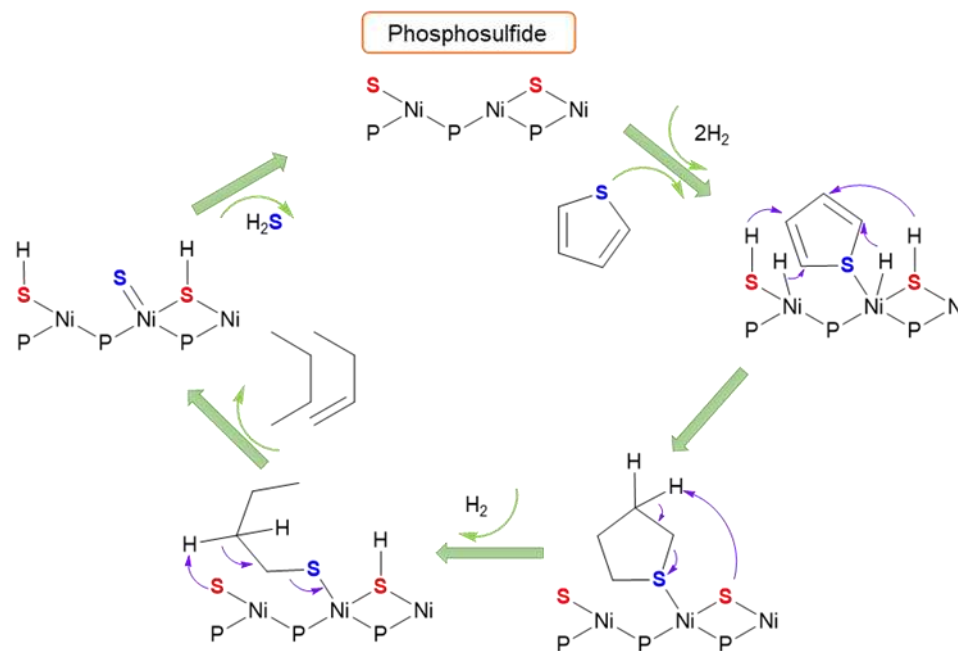


Figure 1.9. Proposed reaction mechanism for hydrodesulfurization on metal phosphides through the phosphosulfide formation routes.

EXAFS studies of spent catalysts have elucidated the reaction intermediates formed during the HDS reaction.¹⁰⁰ After reaction using Ni₂P as the catalyst, a decrease in the Ni-Ni distance occurs, which is due to the formation of a new Ni-S feature.¹⁰⁰ However, since nickel sulfide is not considered a superior HDS catalyst, it is doubtful that the intermediate is predominantly nickel sulfide.¹⁰⁰ Instead, it is suggested that the active phase involves a phosphosulfide (Figure 1.9).¹⁰⁰ This result is supported by a computational calculation that confirmed the formation of a phosphosulfide phase.¹⁰¹ The mechanism of the HDS reaction of thiophene using metal phosphide catalysts has been extensively studied by in-situ quick X-ray absorption fine structure (QXAFS) and FTIR. The QXAFS also shows the formation of either

phosphosulfide or NiPS on the surface that not only provide active sites for HDS but also serve as a protective layer to prevent corrosion or sulfidation.¹⁰² Depicted in Figure 1.9, the sulfur layer in NiPS is thought to catalyze the HDS reaction due to the observed increase in activity when the catalyst was pretreated with H₂S.¹⁰³ This trend is also observed in MoP, where the HDS activity increases during a time-on-stream study, which indicated S-promoted catalysis.¹⁰⁴ Simultaneous time-resolved (STR) IR provides evidence of tetrahydrothiophene (THT) formation but only after a significant amount of Ni-S species forms. The sulfur in NiPS can also facilitate the reaction by capturing and donating hydrogen during the reaction.¹⁰² DFT work on MoP(001) confirms that surface S promotes thiophene HDS and opens up a new pathway for simultaneous C-S bond scission.¹⁰⁵

The mechanism for HDN using metal phosphides has also been explored by studying the reactivity of a heterocyclic nitrogen compound piperidine, and its derivatives, in the presence of 3000 ppm S.¹⁰⁶ These compounds are selected because of the variety of α -H and β -H in the molecules. Based on the product distribution from each reaction, the mechanism of HDN is proposed to go through a S_N2 pathway for less substituted amines, while the more substituted amines proceeded through an E2 elimination pathway.¹⁰⁶ Based on a similar study, the role of β -H is significant only in tertiary α -C alkylamines because the HDN reaction proceeds through an E2 elimination, in which the β -H becomes crucial as molecules with fewer β -H are more favorable.¹⁰⁷ Adsorption energies have been calculated using DFT by comparing the thermodynamics of hydrogenation

steps versus C-N bond cleavage on steps of MoP (010).¹⁰⁸ From these calculations, the most favorable pathway of pyridine HDN occurs via hydrogenation of the aromatics followed by C-N bond cleavage.¹⁰⁸ This calculation result confirmed the report twenty four years prior on HDN of various aromatic amine molecules.¹⁰⁹

The support also affects the catalytic performance of transition metal phosphides. Ni₂P supported on SiO₂ exhibits a higher activity compared to one supported on Al₂O₃ due to the aforementioned AlPO₄ formation.⁶⁵ The M/P ratio also contributes to the activity of the phosphide. For instance, supported Ni₂P is more active than Ni₁₂P₅,⁶⁵ but CoP has a higher activity compared to the more metal rich Co₂P.¹¹⁰ Incorporation of a second metal by doping Ti, Zn, or Ca in Ni₂P while maintaining the bulk phase of Ni₂P enhances the HDS activity.¹¹¹

1.4.2 Hydrogen evolution reaction (HER)

Hydrogen from renewable sources (i.e. water) is a potential clean energy source due to its high energy content. A couple of the challenges that motivate the need of new catalysts for HER are the high cost of noble metal catalysts with near zero overpotential that currently are used in the industry and the short lifetime of electrode materials.¹¹² In HER catalysts, two types of sites are important: a hydride acceptor site and a proton acceptor site. The hydride acceptor is generally any positively charged metal that provides a site for H₂ adsorption, while the proton acceptor is a negatively charged species that captures protons.¹¹³ Another important feature in the HER catalyst is the

hydrogen adsorption and desorption ability of the active sites, which has been observed in phosphide catalysts in HDS, HDN, HDO, and water-gas shift reactions.^{88, 114} Therefore, transition metal phosphides offer a promising alternative to expensive noble metals providing low overpotential and stability. Further, a computational study predicted Ni₂P(001) to be an active HER catalyst because the HER mechanism is similar to the HDS reaction mechanism, where both reactions require adsorption of H₂ on the surface followed by reversible desorption.⁹⁰⁻⁹¹ The claim was later proven correct by sufficient experimental evidence in the field possibly due to an ensemble effect that is provided to the material through the addition of P atom.

The general HER mechanism in acidic media is well understood, while the mechanism in alkaline media is still unclear.¹¹⁵ The first step is the Volmer step where an electron on the catalyst surface captures a proton to produce a hydrogen atom adsorbed on the surface (H_{ads}). The second step could progress through two different pathways depending the level of surface saturation by H_{ads}. When the surface is saturated with H_{ads}, the Tafel reaction proceeds with another H_{ads} to form H₂. Meanwhile, if the surface is not saturated, H_{ads} reacts with a proton and an electron to yield H₂. The experimental Tafel slope is calculated by plotting Equation 1.1 and is compared with the theoretical Tafel slope to suggest a possible HER mechanism for a particular catalyst.¹¹⁵

$$\eta = b \log (j/j_0) \quad \text{(Equation 1.1)}$$

Where η is the overpotential, b is the Tafel slope, j is the current density, and j_0 is the exchange current rate. While the Tafel slope signifies the possible catalytic HER mechanism, the exchange current rate, j_0 , describes the current of the electrode catalyst materials in absence of overpotential.¹¹⁵⁻¹¹⁶ An ideal HER catalyst would show a low Tafel slope and high current density. The mechanism and the Tafel slope for each step is summarized in Table 1.1.

Although the synthesis of nanoparticle metal phosphides has been studied since 2007, it was not until six years later that phosphide catalysts (i.e. FeP) with ~ 0.1 V overpotential and ~ 67 mV/decade Tafel slope were reported for HER.¹¹⁷ Hollow Ni_2P synthesized from the decomposition of TOP has also been reported catalytically active under acidic conditions (0.5 M H_2SO_4) likely due to the exposure of the high density $\text{Ni}_2\text{P}(001)$ surface that was previously predicted to have high activity for HER with reported overpotential of 130 mV for a current density of 20 mA cm^{-2} .¹¹⁸ After 500 cycles, the overpotential required to achieve the same current density increased by less than 25 mV.¹¹⁸ Ni_2P is unstable in 1.0 M KOH, and the material quickly degrades into metallic Ni at this condition.¹¹⁸ Cobalt phosphide, CoP, in 0.5 M H_2SO_4 prepared from thermal decomposition of TOP with the metal precursor has a lower overpotential of ~ 85 mV at 20 mA cm^{-2} compared to Ni_2P .¹¹⁹ The stability of CoP is significant, however, as the activity is unchanged after 4 cycles.¹¹⁹ Co_2P on Ti foil shows only ca. 10% decrease in current density after 1000 cycles.¹²⁰ Molybdenum phosphide (MoP) was also tested for water HER to yield a current density of 30 mA cm^{-2} at an overpotential of 0.18 V with a Tafel slope of 54 mV/decade under the same acidic conditions

(0.5 M H₂SO₄) as mentioned earlier. Similar to CoP, MoP is also not stable in a 1 M KOH reaction medium.¹²¹

The role of the metal:phosphorus ratio was examined with a variety of nickel phosphides (Ni₁₂P₅, Ni₂P, and Ni₅P₄) synthesized from the thermal decomposition of the metal precursor and TOP.¹²² At a current density of 10 mA cm⁻², the onset potential is 80, 62, and 34 mV for Ni₁₂P₅, Ni₂P, and Ni₅P₄, respectively.¹²² Even at low current density, Ni₅P₄ showed the highest potential.¹²² Similar trends are observed for Mo:P catalysts, where MoP exhibits a lower Tafel slope compared to Mo₃P as well as CoP that has lower overpotential compared to its metal rich phase Co₂P.^{121, 123} The results suggest that ensemble effects might play an important role in determining the optimum M:P ratio for different metal.⁹⁰

Co_xFe_{2-x}P is also used as a catalyst for HER to compare to the noble metal based industrial catalysts Pt/C and IrO₂.¹²⁴ Particularly, (Co_{0.52}Fe_{0.48})₂P shows outstanding performance with a low onset potential of ~12 mV, 10 mA cm⁻², and a Tafel slope of 45 mV/decade in 0.5 M H₂SO₄.¹²⁴ In an alkaline solution of 1.0 M KOH, (Co_{0.52}Fe_{0.48})₂P has a low onset potential of 30 mV, a Tafel slope of 40 mV, and a current density of 0.12 mA cm⁻², which exceeds the commercial Pt/C catalyst that has a Tafel slope of 51 mV/decade.¹²⁴ Additionally, at higher current density, the overpotential of (Co_{0.52}Fe_{0.48})₂P is lower than Pt/C, indicating that (Co_{0.52}Fe_{0.48})₂P in alkaline solutions exceeds the HER catalytic performance of Pt/C.¹²⁴

In conclusion, transition metal phosphides have high potential as catalysts for HER in acidic and alkaline media. Optimum M:P ratio is important in determining the most efficient HER catalyst. Bimetallic phosphides $(\text{Co}_{0.52}\text{Fe}_{0.48})_2\text{P}$ have a lower Tafel slope compared to the industrial catalyst Pt/C, which makes this material, and many other bimetallic catalysts, attractive for further evaluation.

1.4.3 Biomass conversion

As mentioned in the beginning of this chapter, biomass can be converted into other chemicals and fuels through catalytic reactions. Phosphide catalysts have been used in several biomass upgrading reactions. Unsupported MoP has higher turnover frequencies (TOFs) than MoS_2 , MoO_2 , and MoO_3 for 4-methylphenol HDO due to the increase in electron density around the Mo atom based on XPS binding energy comparisons.⁴⁹ Several SiO_2 supported monometallic phosphides synthesized through the phosphate precursor TPR method have been examined for guaiacol HDO, and the TOF normalized on CO-accessible sites decreases in the following order at 300°C: $\text{Ni}_2\text{P} > \text{Co}_2\text{P} > \text{Fe}_2\text{P}$, WP, MoP.¹²⁵ At short contact times, guaiacol HDO yields predominantly catechol and small amounts of phenol with Co_2P and WP, while Ni_2P produces a mixture of methoxybenzene, cresol, and benzene.¹²⁵ Citric acid, which forms complexes with Mo, can be added in the synthesis of unsupported MoP to improve the surface area to increase the CO-accessible sites for 4-methylphenol HDO.⁶³

Noble metal phosphides have been tested for furan HDO that could either produce C4 and water or C3 and CO. RuP and Ru₂P improve the HDO ability of Ru as supported Ru catalysts preferred the C-C bond cleavage products (C3 and CO).¹²⁶ In a mechanistic study on Ru(0001) and P_x-Ru(0001), the presence of P on the surface significantly enhances formic acid decomposition.¹²⁷ The incorporation of P decreases the desorption temperature of various probe molecules (CO and NH₃), which implies the electron transfer between Ru(0001) and P inhibits the electron interactions between adsorbates and Ru(0001) surface.¹²⁷ The phosphided Ru(0001) samples prefer C-O bond cleavage of formic acid to form CO and H₂O compared to C-H bond cleavage on the Ru(0001) surface.¹²⁷

The effects associated with supporting transition metal phosphides for HDO of guaiacol have been studied using Ni₂P supported on ZrO₂, Al₂O₃, and SiO₂. The HDO activity decreases from ZrO₂, Al₂O₃, and SiO₂ at 300°C.¹²⁸ At low conversion, Ni₂P/SiO₂ favors demethoxylation and DDO products, while Ni₂P on ZrO₂ or Al₂O₃, favors demethylation for guaiacol HDO.¹²⁸

1.5 Catalytic enhancement in bimetallic phosphides

An enhancement in the catalytic properties of metal phosphides can be done by second metal addition to form bimetallic phosphides. In general, the properties of bimetallic catalysts are attributed to the following: (1) geometric effects due to the change in the geometric or ensemble arrangements of the active sites (2) electronic effects due to the change in the electronic properties of

the active sites (3) stabilizing effects from the metal added to the matrix (4) synergistic effects where the two metals participate in reaction chemistry, and/or (5) bi-functionality where each metal serves a distinct purpose during the reaction.⁸ Many of the reports involving bimetallic phosphides have investigated nickel-based bimetallic phosphides, as Ni₂P is one of the most studied phosphides with high activity for HDS. The aforementioned work includes various phases of FeNi phosphides^{76, 99, 129-131}, CoNi phosphides¹³²⁻¹³⁷, and NiMo phosphides.^{66, 138-141} In most literature reports, the second metal addition in Ni-based bimetallic phosphides increased the selectivity to heteroatom removal with aromatic retention although no improvement activity is observed in comparison to monometallic Ni₂P.¹⁴²⁻¹⁴³

Mo-based bimetallic phosphides have been shown as an excellent heteroatom removal catalyst. Electropositive metals such as Mo and W are excellent choices of metals due to their oxophilic nature, which has been correlated with the heteroatom removal ability of the catalysts.²⁰⁻²¹ For example FeMoP has been tested at 400°C and 4.2 MPa H₂ pressure for anisole, phenol, catechol and (2-phenoxyethyl)benzene HDO reactions to demonstrate the material's ability to cleave C-O bonds commonly found in lignin.⁶⁷⁻⁶⁸ Under this condition, the conversions of anisole with FeP, MoP, and FeMoP were 45%, 65%, and 86%, respectively, which exhibited clear improvement for the bimetallic material. Combinations of the physical mixture of FeP and MoP were also not as effective as the FeMoP catalyst. Additionally, at 400°C, 2.1 MPa H₂ for 3 h, ~99% conversion was achieved for all model compounds with high (>90%)

benzene selectivity using either anisole or phenol as reactants.⁶⁷ HDO of (2-phenoxyethyl)benzene resulted in 85% total deoxygenated compounds while preserving the aromaticity of the reactant.⁶⁷

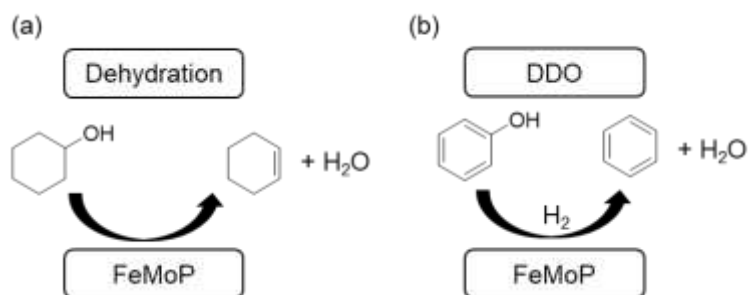


Figure 1.10. (a) Cyclohexanol dehydration and (b) phenol HDO on FeMoP catalyst.

The active sites of FeMoP were probed using cyclohexanol dehydration and phenol HDO as probe reactions with materials synthesized at three different temperatures 650°C, 750°C, and 850°C (Figure 1.10).⁶⁸ The initial reaction rates of dehydration of cyclohexanol were performed in a flow reactor at 5.2 MPa with temperatures ranging from 180°C - 220°C and were normalized with respect to the total acid sites to yield similar normalized rates.⁶⁸ This result implied surface acid sites (Lewis or Brønsted) are the primary sites for cyclohexanol dehydration on the catalyst surface.⁶⁸ The reaction rates of phenol HDO evaluated between 350°C - 400°C were obtained and normalized with respect to CO-titrated sites to yield a similar reaction rates that suggested CO-titrated sites as the main sites for HDO.⁶⁸ At higher conversions, the catalysts synthesized at higher temperatures experienced a sharper decrease in selectivity to the DDO product possibly due to

the loss of Lewis acid sites.⁶⁸ The FeMoP was optimized even further by tuning the Fe:Mo ratio in $\text{Fe}_x\text{Mo}_{2-x}\text{P}$ where the $x = 0.99 - 1.14$ materials exhibited excellent $\text{C-O}_{\text{aromatic}}$ selectivity (i.e., 90%).¹⁴⁴ DFT calculations suggested that the Lewis acid nature in FeMoP drives the selectivity towards $\text{C-O}_{\text{aromatic}}$ bond scission.¹⁴⁴

The stability of FeMoP is excellent. A 48 h time-on-stream (TOS) study of phenol HDO as well as water pulsing experiments in which water was flowed for 15 mins into the system during the TOS study verified the durability of the catalyst.⁶⁸ Both stability studies shows that FeMoP is able to retain its activity and selectivity throughout the experiments, which is remarkably more stable than the monometallic $\text{Ni}_2\text{P}/\text{SiO}_2$, MoP/SiO_2 , and bimetallic $\text{NiMoP}/\text{SiO}_2$ that deactivates possibly due to surface oxidation from water formation.^{68, 143}

Overall, HDO using phosphide catalysts is a promising area with more attention needed primarily due to the difficulty in selectively cleaving C-O bonds present in biomass-based feedstocks. However, there are many others phosphides that have not been tested for these reactions and potentially have superior catalytic performance.

1.6 Dissertation organization

The molecular diversity in biomass feeds poses a challenge for catalytic biomass upgrading processes. Namely, catalysts that could selectively promote simultaneous reactions from different feed compositions are desired. Metal phosphides are understudied materials with high catalytic potential for biomass

upgrading reactions due to its thermal stability and nature of active sites. Further improvement of the material can be obtained with metal addition to form bimetallic phosphides. However, there is still a lack of knowledge in the catalytic potential of bimetallic phosphides for biomass upgrading reactions. Moreover, fundamental understanding towards the structure-reaction relationship is also needed to aid the catalyst design and synthesis for the desired reactions. Therefore, this dissertation addresses these issues through the evaluation of bimetallic phosphides for various reactions pertinent to biomass upgrading.

This dissertation is divided into 7 chapters. **Chapter 2** discusses the theories behind the characterization techniques as well as other experimentation methods used in the studies. **Chapter 3** explores the catalytic consequence of metal substitutions in Mo-based bimetallic phosphides with the focus of correlating the relative oxidation of the surface with the reactivity towards phenol HDO reaction. **Chapter 4** presents a detailed kinetics of bimetallic RuMoP as hydrogenation catalysts for furfural hydrogenation. These results motivate the studies in **Chapter 5** on testing bimetallic RuMoP for the reduction of functionalized aromatics that are relevant in biomass feed. This study also illuminates the nature of the active sites for RuMoP. **Chapter 6** explores the utilization of bimetallic RuMoP and NiMoP for reduction of molecules with competing functionalities such as C=C and C=O bonds in cinnamaldehyde using a combination of experimental, surface science, and theory. Finally, **Chapter 7** provides a conclusion to the dissertation as well as the future direction on this research topic.

1.7 References

1. Bonita, Y.; Hicks, J. C., Metal phosphides and their applications in catalysis. In *Alternative catalytic materials: carbides, nitrides, phosphides, and amorphous boron alloys*, Hargreaves, J. S. J.; McFarlane, A. R.; Kaassiri, S., Eds. Royal Society of Chemistry: Croydon, UK, 2018.
2. Bozell, J. J.; Petersen, G. R., Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited. *Green Chem.* **2010**, *12* (4), 539-554.
3. Huber, G. W.; Iborra, S.; Corma, A., Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem. Rev.* **2006**, *106* (9), 4044-4098.
4. Elliott, D. C., Historical developments in hydroprocessing bio-oils. *Energ. Fuel* **2007**, *21* (3), 1792-1815.
5. Mohan, D.; Pittman, C. U.; Steele, P. H., Pyrolysis of wood/biomass for bio-oil: A critical review. *Energ. Fuel* **2006**, *20* (3), 848-889.
6. Zhou, X.; Broadbelt, L. J.; Vinu, R., Mechanistic understanding of thermochemical conversion of polymers and lignocellulosic biomass. In *Advances in Chemical Engineering*, Van Geem, K. M., Ed. Academic Press: 2016; Vol. 49, pp 95-198.
7. Cheng, J. J.; Timilsina, G. R., Status and barriers of advanced biofuel technologies: A review. *Renewable Energy* **2011**, *36* (12), 3541-3549.
8. Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A., Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chem. Soc. Rev.* **2012**, *41* (24), 8075-8098.
9. Molino, A.; Chianese, S.; Musmarra, D., Biomass gasification technology: The state of the art overview. *Journal of Energy Chemistry* **2016**, *25* (1), 10-25.
10. Hicks, J. C., Advances in C-O Bond Transformations in Lignin-Derived Compounds for Biofuels Production. *J. Phys. Chem. Lett.* **2011**, *2* (18), 2280-2287.
11. Czernik, S.; Bridgwater, A. V., Overview of applications of biomass fast pyrolysis oil. *Energ. Fuel* **2004**, *18* (2), 590-598.
12. Branca, C.; Giudicianni, P.; Di Blasi, C., GC/MS characterization of liquids generated from low-temperature pyrolysis of wood. *Ind. Eng. Chem. Res.* **2003**, *42* (14), 3190-3202.

13. Diebold, J. P. *A review of the chemical and physical mechanism of the storage stability of fast pyrolysis bio-oils*. NREL/SR-570-27613; National Renewable Energy Laboratory: Golden, Colorado, 2000.
14. Wyman, C. E., Ethanol from lignocellulosic biomass: Technology, economics, and opportunities. *Bioresource Technology* **1994**, *50* (1), 3-15.
15. Isikgor, F. H.; Becer, C. R., Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polymer Chemistry* **2015**, *6* (25), 4497-4559.
16. Garrote, G.; Cruz, J. M.; Moure, A.; Domínguez, H.; Parajó, J. C., Antioxidant activity of byproducts from the hydrolytic processing of selected lignocellulosic materials. *Trends in Food Science & Technology* **2004**, *15* (3), 191-200.
17. Furimsky, E., Catalytic hydrodeoxygenation. *Appl. Catal. A* **2000**, *199* (2), 147-190.
18. He, Y.; Laursen, S., The surface and catalytic chemistry of the first row transition metal phosphides in deoxygenation. *Catal. Sci. Technol.* **2018**, *8* (20), 5302-5314.
19. de Souza, P. M.; Nie, L.; Borges, L. E. P.; Noronha, F. B.; Resasco, D. E., Role of oxophilic supports in the selective hydrodeoxygenation of m-cresol on Pd catalysts. *Catal. Lett.* **2014**, *144* (12), 2005-2011.
20. Tan, Q. H.; Wang, G. H.; Long, A.; Dinse, A.; Buda, C.; Shabaker, J.; Resasco, D. E., Mechanistic analysis of the role of metal oxophilicity in the hydrodeoxygenation of anisole. *J. Catal.* **2017**, *347*, 102-115.
21. Robinson, A.; Ferguson, G. A.; Gallagher, J. R.; Cheah, S.; Beckham, G. T.; Schaidle, J. A.; Hensley, J. E.; Medlin, J. W., Enhanced hydrodeoxygenation of m-cresol over bimetallic Pt-Mo catalysts through an oxophilic metal-induced tautomerization pathway. *ACS Catal.* **2016**, *6* (7), 4356-4368.
22. Wu, L.; Moteki, T.; Gokhale, Amit A.; Flaherty, David W.; Toste, F. D., Production of fuels and chemicals from biomass: Condensation reactions and beyond. *Chem* **2016**, *1* (1), 32-58.
23. Schlaf, M., Selective deoxygenation of sugar polyols to α,ω -diols and other oxygen content reduced materials—a new challenge to homogeneous ionic hydrogenation and hydrogenolysis catalysis. *Dalton Transactions* **2006**, (39), 4645-4653.

24. Yinheng, F.; Qiang, W.; Dan, J.; Yunling, Z.; Shijian, L.; Jie, X., Highly selective reaction of cinnamaldehyde to cinnamyl alcohol using nanometric alkali metal hydrides. *Chem. Lett.* **2006**, 35 (5), 488-489.
25. Giroir-Fendler, A.; Richard, D.; Gallezot, P., Chemoselectivity in the catalytic hydrogenation of cinnamaldehyde. Effect of metal particle morphology. *Catal. Lett.* **1990**, 5 (2), 175-181.
26. Yuan, K.; Song, T.; Wang, D.; Zhang, X.; Gao, X.; Zou, Y.; Dong, H.; Tang, Z.; Hu, W., Effective and selective catalysts for cinnamaldehyde hydrogenation: hydrophobic hybrids of metal–organic frameworks, metal nanoparticles, and micro- and mesoporous polymers. *Angewandte Chemie International Edition* **2018**, 57 (20), 5708-5713.
27. Yang, Y. S.; Rao, D. M.; Chen, Y. D.; Dong, S. Y.; Wang, B.; Zhang, X.; Wei, M., Selective hydrogenation of cinnamaldehyde over Co-based intermetallic compounds derived from layered double hydroxides. *ACS Catal.* **2018**, 8 (12), 11749-11760.
28. Li, Y.; Cheng, H.; Lin, W.; Zhang, C.; Wu, Q.; Zhao, F.; Arai, M., Solvent effects on heterogeneous catalysis in the selective hydrogenation of cinnamaldehyde over a conventional Pd/C catalyst. *Catal. Sci. Technol.* **2018**, 8 (14), 3580-3589.
29. Coq, B.; Kumbhar, P. S.; Moreau, C.; Moreau, P.; Warawdekar, M. G., Liquid-phase hydrogenation of cinnamaldehyde over supported ruthenium catalysts - influence of particle-size, bimetallics and nature of support. *J. Mol. Catal.* **1993**, 85 (2), 215-228.
30. Plomp, A. J.; Vuori, H.; Krause, A. O. I.; de Jong, K. P.; Bitter, J. H., Particle size effects for carbon nanofiber supported platinum and ruthenium catalysts for the selective hydrogenation of cinnamaldehyde. *Applied Catalysis A: General* **2008**, 351 (1), 9-15.
31. Goupil, D.; Fouilloux, P.; Maurel, R., Activity and selectivity of Pt-Fe/C alloys for the liquid phase hydrogenation of cinnamaldehyde to cinnamyl alcohol. *React. Kinet. Catal. Lett.* **1987**, 35 (1-2), 185-193.
32. Koo-amornpattana, W.; Winterbottom, J. M., Pt and Pt-alloy catalysts and their properties for the liquid-phase hydrogenation of cinnamaldehyde. *Catal. Today* **2001**, 66 (2), 277-287.
33. Luo, Y.; Li, Z.; Li, X.; Liu, X.; Fan, J.; Clark, J. H.; Hu, C., The production of furfural directly from hemicellulose in lignocellulosic biomass: A review. *Catal. Today* **2019**, 319, 14-24.

34. Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sadaba, I.; Granados, M. L., Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels. *Energ Environ Sci* **2016**, 9 (4), 1144-1189.
35. Lange, J.-P.; van der Heide, E.; van Buijtenen, J.; Price, R., Furfural—A Promising Platform for Lignocellulosic Biofuels. *ChemSusChem* **2012**, 5 (1), 150-166.
36. Thewes, M.; Muether, M.; Pischinger, S.; Budde, M.; Brunn, A.; Sehr, A.; Adomeit, P.; Klankermayer, J., Analysis of the impact of 2-methylfuran on mixture formation and combustion in a direct-injection spark-ignition engine. *Energ. Fuel* **2011**, 25 (12), 5549-5561.
37. Merat, N.; Godawa, C.; Gaset, A., High selective production of tetrahydrofurfuryl alcohol - catalytic hydrogenation of furfural and furfuryl alcohol. *J. Chem. Technol. Biotechnol.* **1990**, 48 (2), 145-159.
38. Sajid, M.; Zhao, X.; Liu, D., Production of 2,5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF): recent progress focusing on the chemical-catalytic routes. *Green Chem.* **2018**, 20 (24), 5427-5453.
39. Robinson, A. M.; Hensley, J. E.; Medlin, J. W., Bifunctional catalysts for upgrading of biomass-derived oxygenates: a review. *ACS Catal.* **2016**, 6 (8), 5026-5043.
40. Greenwood, N. N. E., A., *Chemistry of the elements*. 2 ed.; Butterworth-Heinemann: Boston, 1997.
41. Pelletier, B.; Pelletier, C.; Séddilot, J., Mémoires et Observations de Chimie. *Chez Croullerois* **1798**, 2, 42.
42. Carencu, S.; Portehault, D.; Boissiere, C.; Mezailles, N.; Sanchez, C., Nanoscaled metal borides and phosphides: recent developments and perspectives. *Chem. Rev.* **2013**, 113 (10), 7981-8065.
43. Oyama, S. T.; Gott, T.; Zhao, H. Y.; Lee, Y. K., Transition metal phosphide hydroprocessing catalysts: A review. *Catal. Today.* **2009**, 143 (1-2), 94-107.
44. Buseck, P. R., Phosphide from Meteorites - Barringerite, a New Iron-Nickel Mineral. *Science* **1969**, 165 (3889), 169-&.
45. Britvin, S. N.; Rudashevsky, N. S.; Krivovichev, S. V.; Burns, P. C.; Polekhovsky, Y. S., Allabogdanite, (Fe,Ni)₂P, a new mineral from the Onello meteorite: The occurrence and crystal structure. *Am Mineral* **2002**, 87 (8-9), 1245-1249.

46. Britvin, S. N.; Murashko, M. N.; Vapnik, Y.; Polekhovsky, Y. S.; Krivovichev, S. V., Earth's Phosphides in Levant and insights into the source of Archean prebiotic phosphorus. *Sci. Rep.* **2015**, 5.
47. Fruchart, R.; Roger, A.; Sendteur, J. P., Crystallographic and Magnetic Properties of Solid Solutions of Phosphides M_2P $M=Cr$ Mn Fe Co and Ni . *J Appl Phys* **1969**, 40 (3), 1250-&.
48. Li, D.; Arachchige, M. P.; Kulikowski, B.; Lawes, G.; Seda, T.; Brock, S. L., Control of Composition and Size in Discrete $Co_xFe_{2-x}P$ Nanoparticles: Consequences for Magnetic Properties. *Chem. Mater.* **2016**, 28 (11), 3920-3927.
49. Whiffen, V. M. L.; Smith, K. J., Hydrodeoxygenation of 4-Methylphenol over Unsupported MoP , MoS_2 , and MoO_x Catalysts. *Energ. Fuel* **2010**, 24, 4728-4737.
50. Lee, Y. K.; Oyama, S. T., Bifunctional nature of a SiO_2 -supported Ni_2P catalyst for hydrotreating: EXAFS and FTIR studies. *J. Catal.* **2006**, 239 (2), 376-389.
51. Bonita, Y.; O'Connell, T. P.; Miller, H. E.; Hicks, J. C., Revealing the hydrogenation performance of $RuMo$ phosphide for chemoselective reduction of functionalized aromatic hydrocarbons. *Ind. Eng. Chem. Res.* **2019**, 58 (9), 3650-3658.
52. Basila, M. R.; Kantner, T. R.; Rhee, K. H., The nature of the acidic sites on a silica-alumina. Characterization by infrared spectroscopic studies of trimethylamine and pyridine chemisorption. *J. Phys. Chem.* **1964**, 68 (11), 3197-3207.
53. Yan, K.; Li, Y.; Zhang, X.; Yang, X.; Zhang, N.; Zheng, J.; Chen, B.; Smith, K. J., Effect of preparation method on Ni_2P/SiO_2 catalytic activity for $NaBH_4$ methanolysis and phenol hydrodeoxygenation. *Int J Hydrogen Energ* **2015**, 40 (46), 16137-16146.
54. Usman, M.; Li, D.; Li, C.; Zhang, S., Highly selective and stable hydrogenation of heavy aromatic-naphthalene over transition metal phosphides. *Science China Chemistry* **2015**, 58 (4), 738-746.
55. Maeda, Y.; Takashima, Y., Mossbauer studies of solid solution systems of $Fe(P, as)$, $(Fe, Co)P$, $(Fe, Mn)P$ and $(Fe, W)P$. *J Inorg Nucl Chem* **1973**, 35 (4), 1219-1225.
56. Maeda, Y.; Takashima, Y., Mossbauer studies of $FeNiP$ and related compounds. *J Inorg Nucl Chem* **1973**, 35 (6), 1963-1969.

57. Oyama, S. T.; Zhao, H. Y.; Freund, H. J.; Asakura, K.; Wlodarczyk, R.; Sierka, M., Unprecedented selectivity to the direct desulfurization (DDS) pathway in a highly active FeNi bimetallic phosphide catalyst. *J. Catal.* **2012**, 285 (1), 1-5.
58. Oyama, S. T.; Lee, Y. K., The active site of nickel phosphide catalysts for the hydrodesulfurization of 4,6-DMDBT. *J. Catal.* **2008**, 258 (2), 393-400.
59. Zhang, Y.; Lei, H.; Duan, D.; Villota, E.; Liu, C.; Ruan, R., New insight into the mechanism of the hydrogen evolution reaction on MoP(001) from first principles. *Acs Appl Mater Inter* **2018**, 10 (24), 20429-20439.
60. Prins, R.; Bussell, M. E., Metal Phosphides: Preparation, Characterization and Catalytic Reactivity. *Catal. Lett.* **2012**, 142 (12), 1413-1436.
61. Rodriguez, J. A.; Kim, J. Y.; Hanson, J. C.; Sawhill, S. J.; Bussell, M. E., Physical and chemical properties of MoP, Ni₂P, and MoNiP hydrodesulfurization catalysts: Time-resolved X-ray diffraction, density functional, and hydrodesulfurization activity studies. *J. Phys. Chem. B* **2003**, 107 (26), 6276-6285.
62. Yang, S. F.; Liang, C. H.; Prins, R., A novel approach to synthesizing highly active Ni₂P/SiO₂ hydrotreating catalysts. *J. Catal.* **2006**, 237 (1), 118-130.
63. Whiffen, V. M. L.; Smith, K. J.; Straus, S. K., The influence of citric acid on the synthesis and activity of high surface area MoP for the hydrodeoxygenation of 4-methylphenol. *Appl. Catal. A* **2012**, 419, 111-125.
64. Chen, J. X.; Chen, Y.; Yang, Q.; Li, K. L.; Yao, C. C., An approach to preparing highly dispersed Ni₂P/SiO₂ catalyst. *Catal. Commun.* **2010**, 11 (6), 571-575.
65. Sawhill, S. J.; Layman, K. A.; Van Wyk, D. R.; Engelhard, M. H.; Wang, C.; Bussell, M. E., Thiophene hydrodesulfurization over nickel phosphide catalysts: effect of the precursor composition and support. *J. Catal.* **2005**, 231 (2), 300-313.
66. Sun, F. X.; Wu, W. C.; Wu, Z. L.; Guo, J.; Wei, Z. B.; Yang, Y. X.; Jiang, Z. X.; Tian, F. P.; Li, C., Dibenzothiophene hydrodesulfurization activity and surface sites of silica-supported MoP, Ni₂P, and Ni-Mo-P catalysts. *J. Catal.* **2004**, 228 (2), 298-310.
67. Rensel, D. J.; Rouvimov, S.; Gin, M. E.; Hicks, J. C., Highly selective bimetallic FeMoP catalyst for C-O bond cleavage of aryl ethers. *J. Catal.* **2013**, 305, 256-263.

68. Rensel, D. J.; Kim, J.; Bonita, Y.; Hicks, J. C., Investigating the multifunctional nature of bimetallic FeMoP catalysts using dehydration and hydrogenolysis reactions. *Appl. Catal. A* **2016**, 524, 85-93.
69. Bui, P.; Cecilia, J. A.; Oyama, S. T.; Takagaki, A.; Infantes-Molina, A.; Zhao, H. Y.; Li, D.; Rodriguez-Castellon, E.; Lopez, A. J., Studies of the synthesis of transition metal phosphides and their activity in the hydrodeoxygenation of a biofuel model compound. *J. Catal.* **2012**, 294, 184-198.
70. Carencio, S.; Boissiere, C.; Nicole, L.; Sanchez, C.; Le Floch, P.; Mezailles, N., Controlled Design of Size-Tunable Monodisperse Nickel Nanoparticles. *Chem. Mater.* **2010**, 22 (4), 1340-1349.
71. Chiang, R. K.; Chiang, R. T., Formation of hollow Ni₂P nanoparticles based on the nanoscale Kirkendall effect. *Inorg. Chem.* **2007**, 46 (2), 369-371.
72. Henkes, A. E.; Vasquez, Y.; Schaak, R. E., Converting metals into phosphides: A general strategy for the synthesis of metal phosphide nanocrystals. *J. Am. Chem. Soc.* **2007**, 129 (7), 1896-+.
73. Muthuswamy, E.; Savithra, G. H. L.; Brock, S. L., Synthetic Levers Enabling Independent Control of Phase, Size, and Morphology in Nickel Phosphide Nanoparticles. *ACS Nano* **2011**, 5 (3), 2402-2411.
74. Zheng, X. F.; Yuan, S. L.; Tian, Z. M.; Yin, S. Y.; He, J. H.; Liu, K. L.; Liu, L., One-pot synthesis of hollow nickel phosphide nanoparticles with tunable void sizes using triphenylphosphine. *Mater Lett* **2009**, 63 (27), 2283-2285.
75. Muthuswamy, E.; Kharel, P. R.; Lawes, G.; Brock, S. L., Control of Phase in Phosphide Nanoparticles Produced by Metal Nanoparticle Transformation: Fe₂P and FeP. *ACS Nano* **2009**, 3 (8), 2383-2393.
76. Hitihami-Mudiyanselage, A.; Arachchige, M. P.; Seda, T.; Lawes, G.; Brock, S. L., Synthesis and Characterization of Discrete Fe_xNi_{2-x}P Nanocrystals (0 < x < 2): Compositional Effects on Magnetic Properties. *Chem. Mater.* **2015**, 27 (19), 6592-6600.
77. Guan, Q. X.; Li, W., A novel synthetic approach to synthesizing bulk and supported metal phosphides. *J. Catal.* **2010**, 271 (2), 413-415.
78. Guan, Q. X.; Li, W.; Zhang, M. H.; Tao, K. Y., Alternative synthesis of bulk and supported nickel phosphide from the thermal decomposition of hypophosphites. *J. Catal.* **2009**, 263 (1), 1-3.

79. Wang, J. N.; Chen, H.; Fu, Y. C.; Shen, J. Y., Highly active Ni₂P/SiO₂ catalysts phosphorized by triphenylphosphine in liquid phase for the hydrotreating reactions. *Appl. Catal. B* **2014**, *160*, 344-355.
80. Zhao, Y.; Xue, M. W.; Cao, M. H.; Shen, J. Y., A highly loaded and dispersed Ni₂P/SiO₂ catalyst for the hydrotreating reactions. *Appl. Catal. B* **2011**, *104* (3-4), 229-233.
81. Qian, X. F.; Xie, Y.; Qian, Y. T.; Zhang, X. M.; Wang, W. Z.; Yang, L., Organo-thermal preparation of nanocrystalline cobalt phosphides. *Materials Science and Engineering* **1997**, 135-137.
82. Xie, Y.; Su, H. L.; Qian, X. F.; Liu, X. M.; Qian, Y. T., A mild one-step solvothermal route to metal phosphides (metal = Co, Ni, Cu). *J. Solid State Chem.* **2000**, *149* (1), 88-91.
83. Liu, J. W.; Chen, X. Y.; Shao, M. W.; An, C. H.; Yu, W. C.; Qian, Y. T., Surfactant-aided solvothermal synthesis of dinickel phosphide nanocrystallites using red phosphorus as starting materials. *J. Cryst. Growth* **2003**, *252* (1-3), 297-301.
84. Topsoe, H.; Hinnemann, B.; Norskov, J. K.; Lauritsen, J. V.; Besenbacher, F.; Hansen, P. L.; Hytoft, G.; Egeberg, R. G.; Knudsen, K. G., The role of reaction pathways and support interactions in the development of high activity hydrotreating catalysts. *Catal. Today*. **2005**, *107-08*, 12-22.
85. Gates, B. C.; Topsoe, H., Reactivities in deep catalytic hydrodesulfurization: Challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. *Polyhedron* **1997**, *16* (18), 3213-3217.
86. Houalla, M.; Nag, N. K.; Sapre, A. V.; Broderick, D. H.; Gates, B. C., Hydrodesulfurization of Dibenzothiophene Catalyzed by Sulfided Co-Moo₃-Gamma-Al₂O₃ - Reaction Network. *Aiche J* **1978**, *24* (6), 1015-1021.
87. Vrinat, M. L., The Kinetics of the Hydrodesulfurization Process - a Review. *Appl Catal* **1983**, *6* (2), 137-158.
88. Oyama, S. T., Novel catalysts for advanced hydroprocessing: transition metal phosphides. *J. Catal.* **2003**, *216* (1-2), 343-352.
89. Singhal, G. H.; Espino, R. L.; Sobel, J. E.; Huff, G. A., Hydrodesulfurization of Sulfur Heterocyclic-Compounds - Kinetics of Dibenzothiophene. *J. Catal.* **1981**, *67* (2), 457-468.

90. Liu, P.; Rodriguez, J. A., Catalysts for hydrogen evolution from the [NiFe] hydrogenase to the Ni₂P(001) surface: The importance of ensemble effect. *J. Am. Chem. Soc.* **2005**, *127* (42), 14871-14878.
91. Liu, P.; Rodriguez, J. A.; Asakura, T.; Gomes, J.; Nakamura, K., Desulfurization reactions on Ni₂P(001) and alpha-Mo₂C(001) surfaces: Complex role of P and C sites. *J. Phys. Chem. B* **2005**, *109* (10), 4575-4583.
92. Song, C. S., An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel. *Catal. Today*. **2003**, *86* (1-4), 211-263.
93. Brock, S. L.; Senevirathne, K., Recent developments in synthetic approaches to transition metal phosphide nanoparticles for magnetic and catalytic applications. *J. Solid State Chem.* **2008**, *181* (7), 1552-1559.
94. Sweeny, N. P.; Rohrer, C. S.; Brown, O. W., Dinickel Phosphide as a Heterogeneous Catalyst for the Vapor Phase Reduction of Nitrobenzene with Hydrogen to Aniline and Water. *J. Am. Chem. Soc.* **1958**, *80* (4), 799-800.
95. Nozaki, F.; Kitoh, T.; Sodesawa, T., Promoting Effect of Oxygen for Hydrogenation of Butadiene over Ni₂p Catalyst. *J. Catal.* **1980**, *62* (2), 286-293.
96. Nozaki, F.; Tokumi, M., Hydrogenation Activity of Metal Phosphides and Promoting Effect of Oxygen. *J. Catal.* **1983**, *79* (1), 207-210.
97. Kanda, Y.; Temma, C.; Nakata, K.; Kobayashi, T.; Sugioka, M.; Uemichi, Y., Preparation and performance of noble metal phosphides supported on silica as new hydrodesulfurization catalysts. *Appl. Catal. A* **2010**, *386* (1-2), 171-178.
98. Wang, X. Q.; Clark, P.; Oyama, S. T., Synthesis, characterization, and hydrotreating activity of several iron group transition metal phosphides. *J. Catal.* **2002**, *208* (2), 321-331.
99. Zhao, H. Y.; Oyama, S. T.; Freund, H. J.; Wlndarczyk, R.; Sierka, M., Nature of active sites in Ni₂P hydrotreating catalysts as probed by iron substitution. *Appl. Catal. B* **2015**, *164*, 204-216.
100. Oyama, S. T.; Wang, X.; Lee, Y. K.; Chun, W. J., Active phase of Ni₂P/SiO₂ in hydroprocessing reactions. *J. Catal.* **2004**, *221* (2), 263-273.

101. Nelson, A. E.; Sun, M. Y.; Junaid, A. S. M., On the structure and composition of the phosphosulfide overlayer on Ni₂P at hydrotreating conditions. *J. Catal.* **2006**, *241* (1), 180-188.
102. Bando, K. K.; Wada, T.; Miyamoto, T.; Miyazaki, K.; Takakusagi, S.; Koike, Y.; Inada, Y.; Nomura, M.; Yamaguchi, A.; Gott, T.; Oyama, S. T.; Asakura, K., Combined in situ QXAFS and FTIR analysis of a Ni phosphide catalyst under hydrodesulfurization conditions. *J. Catal.* **2012**, *286*, 165-171.
103. Duan, X. P.; Teng, Y.; Wang, A. J.; Kogan, V. M.; Li, X.; Wang, Y., Role of sulfur in hydrotreating catalysis over nickel phosphide. *J. Catal.* **2009**, *261* (2), 232-240.
104. Phillips, D. C.; Sawhill, S. J.; Self, R.; Bussell, M. E., Synthesis, characterization, and hydrodesulfurization properties of silica-supported molybdenum phosphide catalysts. *J. Catal.* **2002**, *207* (2), 266-273.
105. Li, G. X.; Zhu, H. Y.; Zhao, L. M.; Guo, W. Y.; Ma, H. F.; Yu, Y. C.; Lu, X. Q.; Liu, Y. J., Theoretical survey of the thiophene hydrodesulfurization mechanism on clean and single-sulfur-atom-modified MoP(001). *J. Phys. Chem. C* **2016**, *120* (40), 23009-23023.
106. Oyama, S. T.; Lee, Y. K., Mechanism of hydrodenitrogenation on phosphides and sulfides. *J. Phys. Chem. B* **2005**, *109* (6), 2109-2119.
107. Zhao, Y.; Prins, R., Mechanisms of the hydrodenitrogenation of alkylamines with secondary and tertiary alpha-carbon atoms on sulfided NiMo/Al₂O₃. *J. Catal.* **2004**, *222* (2), 532-544.
108. Deng, Z. G.; Lei, Y. Q.; Lu, X. Q.; Wang, W. L.; Zhu, H. Y.; Ng, S. P.; Guo, W. Y.; Wu, C. M. L., Hydrodenitrogenation of pyridine on MoP(010): Competition between hydrogenation and denitrification. *Inorg Chim Acta* **2015**, *435*, 30-37.
109. Perot, G., The reactions involved in hydrodenitrogenation. *Catal. Today.* **1991**, *10* (4), 447-472.
110. Burns, A. W.; Layman, K. A.; Bale, D. H.; Bussell, M. E., Understanding the relationship between composition and hydrodesulfurization properties for cobalt phosphide catalysts. *Appl. Catal. A* **2008**, *343* (1-2), 68-76.
111. Zhang, F. Y.; Song, H.; Song, H. L.; Li, F.; Chen, Y. G., Preparation of metal (Ti, Zn and Ca) modified Ni₂P catalysts and HDS performance and kinetic studies. *J Taiwan Inst Chem E* **2016**, *65*, 558-564.

112. Strmcnik, D.; Lopes, P. P.; Genorio, B.; Stamenkovic, V. R.; Markovic, N. M., Design principles for hydrogen evolution reaction catalyst materials. *Nano Energy* **2016**, 29, 29-36.
113. Huang, Z. P.; Chen, Z. B.; Chen, Z. Z.; Lv, C. C.; Meng, H.; Zhang, C., Ni₁₂P₅ Nanoparticles as an Efficient Catalyst for Hydrogen Generation via Electrolysis and Photoelectrolysis. *ACS Nano* **2014**, 8 (8), 8121-8129.
114. Liu, P.; Rodriguez, J. A.; Takahashi, Y.; Nakamura, K., Water-gas-shift reaction on a Ni₂P(001) catalyst: Formation of oxy-phosphides and highly active reaction sites. *J. Catal.* **2009**, 262 (2), 294-303.
115. Zou, X. X.; Zhang, Y., Noble metal-free hydrogen evolution catalysts for water splitting. *Chem. Soc. Rev.* **2015**, 44 (15), 5148-5180.
116. Shi, Y. M.; Zhang, B., Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction. *Chem. Soc. Rev.* **2016**, 45 (6), 1529-1541.
117. Xu, Y.; Wu, R.; Zhang, J. F.; Shi, Y. M.; Zhang, B., Anion-exchange synthesis of nanoporous FeP nanosheets as electrocatalysts for hydrogen evolution reaction. *Chem. Commun.* **2013**, 49 (59), 6656-6658.
118. Popczun, E. J.; McKone, J. R.; Read, C. G.; Biacchi, A. J.; Wiltout, A. M.; Lewis, N. S.; Schaak, R. E., Nanostructured Nickel Phosphide as an Electrocatalyst for the Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2013**, 135 (25), 9267-9270.
119. Popczun, E. J.; Read, C. G.; Roske, C. W.; Lewis, N. S.; Schaak, R. E., Highly Active Electrocatalysis of the Hydrogen Evolution Reaction by Cobalt Phosphide Nanoparticles. *Angew. Chem. Int. Edit.* **2014**, 53 (21), 5427-5430.
120. Huang, Z. P.; Chen, Z. Z.; Chen, Z. B.; Lv, C. C.; Humphrey, M. G.; Zhang, C., Cobalt phosphide nanorods as an efficient electrocatalyst for the hydrogen evolution reaction. *Nano Energy* **2014**, 9, 373-382.
121. Xiao, P.; Sk, M. A.; Thia, L.; Ge, X. M.; Lim, R. J.; Wang, J. Y.; Lim, K. H.; Wang, X., Molybdenum phosphide as an efficient electrocatalyst for the hydrogen evolution reaction. *Energ Environ Sci* **2014**, 7 (8), 2624-2629.
122. Pan, Y.; Liu, Y.; Zhao, J.; Yang, K.; Liang, J.; Liu, D.; Hu, W.; Liu, D.; Liu, Y.; Liu, C., Monodispersed nickel phosphide nanocrystals with different phases: synthesis, characterization and electrocatalytic properties for hydrogen evolution. *J Mater Chem A* **2014**, 3 (1656).

123. Callejas, J. F.; Read, C. G.; Popczun, E. J.; McEnaney, J. M.; Schaak, R. E., Nanostructured Co₂P Electrocatalyst for the Hydrogen Evolution Reaction and Direct Comparison with Morphologically Equivalent CoP. *Chem. Mater.* **2015**, 27 (10), 3769-3774.
124. Tan, Y. W.; Wang, H.; Liu, P.; Shen, Y. H.; Cheng, C.; Hirata, A.; Fujita, T.; Tang, Z.; Chen, M. W., Versatile nanoporous bimetallic phosphides towards electrochemical water splitting. *Energ. Environ. Sci.* **2016**, 9 (7), 2257-2261.
125. Zhao, H. Y.; Li, D.; Bui, P.; Oyama, S. T., Hydrodeoxygenation of guaiacol as model compound for pyrolysis oil on transition metal phosphide hydroprocessing catalysts. *Appl. Catal. A* **2011**, 391 (1-2), 305-310.
126. Bowker, R. H.; Smith, M. C.; Pease, M. L.; Slenkamp, K. M.; Kovarik, L.; Bussell, M. E., Synthesis and hydrodeoxygenation properties of ruthenium phosphide catalysts. *ACS Catal.* **2011**, 1 (8), 917-922.
127. Chang, S. A.; Flaherty, D. W., Mechanistic Study of Formic Acid Decomposition over Ru(0001) and P-X-Ru(0001): Effects of Phosphorus on C-H and C-O Bond Rupture. *J. Phys. Chem. C* **2016**, 120 (44), 25425-25435.
128. Wu, S. K.; Lai, P. C.; Lin, Y. C.; Wan, H. P.; Lee, H. T.; Chang, Y. H., Atmospheric Hydrodeoxygenation of Guaiacol over Alumina-, Zirconia-, and Silica-Supported Nickel Phosphide Catalysts. *ACS Sustain. Chem. Eng.* **2013**, 1 (3), 349-358.
129. Singh, B.; Ho, C. L.; Tseng, Y. C.; Lo, C. T., Controlled synthesis and magnetic properties of nickel phosphide and bimetallic iron-nickel phosphide nanorods. *J Nanopart Res* **2012**, 14 (2).
130. Balli, M.; Fruchart, D.; Gignoux, D.; Tobola, J.; Hlil, E. K.; Wolfers, P.; Zach, R., Magnetocaloric effect in ternary metal phosphides (Fe_{1-x}Ni_x)(2)P. *J Magn Magn Mater* **2007**, 316 (2), 358-360.
131. Ma, Z. Z.; Li, R. X.; Wang, M.; Meng, H. J.; Zhang, F.; Bao, X. Q.; Tang, B.; Wang, X. G., Self-supported porous Ni-Fe-P composite as an efficient electrocatalyst for hydrogen evolution reaction in both acidic and alkaline medium. *Electrochim Acta* **2016**, 219, 194-203.
132. Danforth, S. J.; Liyanage, D. R.; Hitihami-Mudiyanselage, A.; Ilic, B.; Brock, S. L.; Bussell, M. E., Probing hydrodesulfurization over bimetallic phosphides using monodisperse Ni₂-xM_xP nanoparticles encapsulated in mesoporous silica. *Surf. Sci.* **2016**, 648, 126-135.

133. Liyanage, D. R.; Danforth, S. J.; Liu, Y.; Bussell, M. E.; Brock, S. L., Simultaneous Control of Composition, Size, and Morphology in Discrete Ni₂-xCoxP Nanoparticles. *Chem. Mater.* **2015**, 27 (12), 4349-4357.
134. Li, W.; Gao, X. F.; Wang, X. G.; Xiong, D. H.; Huang, P. P.; Song, W. G.; Bao, X. Q.; Liu, L. F., From water reduction to oxidation: Janus Co-Ni-P nanowires as high-efficiency and ultrastable electrocatalysts for over 3000 h water splitting. *J Power Sources* **2016**, 330, 156-166.
135. Fu, S. F.; Zhu, C. Z.; Song, J. H.; Engelhard, M. H.; Li, X. L.; Du, D.; Lin, Y. H., Highly ordered mesoporous bimetallic phosphides as efficient oxygen evolution electrocatalysts. *ACS Energy Lett.* **2016**, 1 (4), 792-796.
136. Wang, B. H. X. Z., Z.; Huang, H.; Dai, J., Hydrothermal synthesis of cobalt-nickel bimetallic phosphides. *Applied Nanoscience* **2012**, 2, 481-485.
137. Yu, J.; Li, Q. Q.; Li, Y.; Xu, C. Y.; Zhen, L.; Dravid, V. P.; Wu, J. S., Ternary Metal Phosphide with Triple-Layered Structure as a Low-Cost and Efficient Electrocatalyst for Bifunctional Water Splitting. *Adv. Funct. Mater.* **2016**, 26 (42), 7644-7651.
138. Stinner, C.; Prins, R.; Weber, T., Binary and ternary transition-metal phosphides as HDN catalysts. *J. Catal.* **2001**, 202 (1), 187-194.
139. Wang, R.; Smith, K. J., Hydrodesulfurization of 4,6-dimethyldibenzothiophene over high surface area metal phosphides. *Appl. Catal. A* **2009**, 361 (1-2), 18-25.
140. Wang, R.; Smith, K. J., Preparation of Unsupported NiMoP Catalysts for 4,6-Dimethyldibenzothiophene Hydrodesulfurization. *Catal. Lett.* **2014**, 144 (9), 1594-1601.
141. Ma, D.; Xiao, T. C.; Xie, S. H.; Zhou, W. Z.; Gonzalez-Cortes, S. L.; Green, M. L. H., Synthesis and structure of bimetallic nickel molybdenum phosphide solid solutions. *Chem. Mater.* **2004**, 16 (14), 2697-2699.
142. Cho, A.; Shin, J.; Takagaki, A.; Kikuchi, R.; Oyama, S. T., Ligand and ensemble effects in bimetallic NiFe phosphide catalysts for the hydrodeoxygenation of 2-methyltetrahydrofuran. *Top. Catal.* **2012**, 55 (14-15), 969-980.
143. Li, K. L.; Wang, R. J.; Chen, J. X., Hydrodeoxygenation of Anisole over Silica-Supported Ni₂P, MoP, and NiMoP Catalysts. *Energ. Fuel* **2011**, 25 (3), 854-863.

144. Rensel, D. J.; Kim, J.; Jain, V.; Bonita, Y.; Rai, N.; Hicks, J. C.,
Composition-directed $\text{Fe}_x\text{Mo}_{2-x}\text{P}$ bimetallic catalysts for
hydrodeoxygenation reactions. *Catal. Sci. Technol.* **2017**, 7, 1857-1867.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Chapter overview

This chapter provides an overview of all the characterization techniques that are used throughout the study.

2.2 Powder x-ray diffraction

Powder x-ray diffraction (XRD) is used to confirm the crystal structure of the materials post-synthesis. This technique uses an x-ray source with a known wavelength on the crystalline samples to obtain information about the atom arrangements in the crystal structures. Usually slits are placed after the x-ray source to limit the electrons that can reach the samples. When the x-ray hit the atoms of the sample, the x-ray diffracts or scatters. The diffracted x-ray is captured by the detector.

The signal counts in XRD depends on constructive and destructive interference of the diffracted x-ray. The destructively interfering spots do not result in XRD signal. However, the constructively interfering spots produces XRD signals. Assuming that the distance between the atoms (d-spacing) are arranged

periodically and the incoming x-ray comes with a known angle (θ), the wavelength of the incoming x-ray follows the Bragg angle (Equation 2.1)¹.

$$n\lambda = 2 d \sin \theta \quad (\text{Equation 2.1})$$

The crystallite size can also be estimated with Scherrer equation (Equation 2.2) where τ is the crystallite size, λ is the wavelength of the incoming x-ray, β is full width half maximum of the chosen peak, θ is the Bragg angle of the chosen peak, and K is the shape factor (0.90 is commonly used). However, this equation must be used with caution.

$$\tau = \frac{K \lambda}{\beta \cos \theta} \quad (\text{Equation 2.2})$$

2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is used to observe the chemical state of the samples. In XPS, x-ray beam with a known energy is illuminated on the sample. When the x-ray hits the sample, the photoelectron effect takes place and the core electron is ejected from the sample. The energy of these electrons is then captured by the detector. The energy captured by the detector (KE) is defined as the input x-ray energy ($h\nu$) subtracted by the binding energy (BE) and work function of the instrument (ϕ).

$$KE = h\nu - BE + \phi \quad (\text{Equation 2.3})$$

Thus, the BE can be defined as the energy required to eject a core electron. The shift in BE signifies the oxidation state of the material. This BE is for the most part distinct for each element. The binding energy of the C 1s peak is usually shifted to 284.8 eV to eliminate shift from the instrument. However, some elements such as Ru 3d overlaps with the C 1s.

To overcome this issue, we developed methods using other elements such as Ni or Cu as XPS standard. For Ni standard, metallic Ni powder is physically mixed with the sample and the Ni 2p_{3/2} peak is shifted to 853.0 eV. For Cu standard, Cu-foil is placed on a tape, while the samples are placed around the Cu-foil. The XPS spectra collection must include at least ~10% of the Cu-foil in the secondary electron image (SEI) area. Additionally, Ar sputtering is employed to remove surface oxidation on the Cu-foil and the samples.

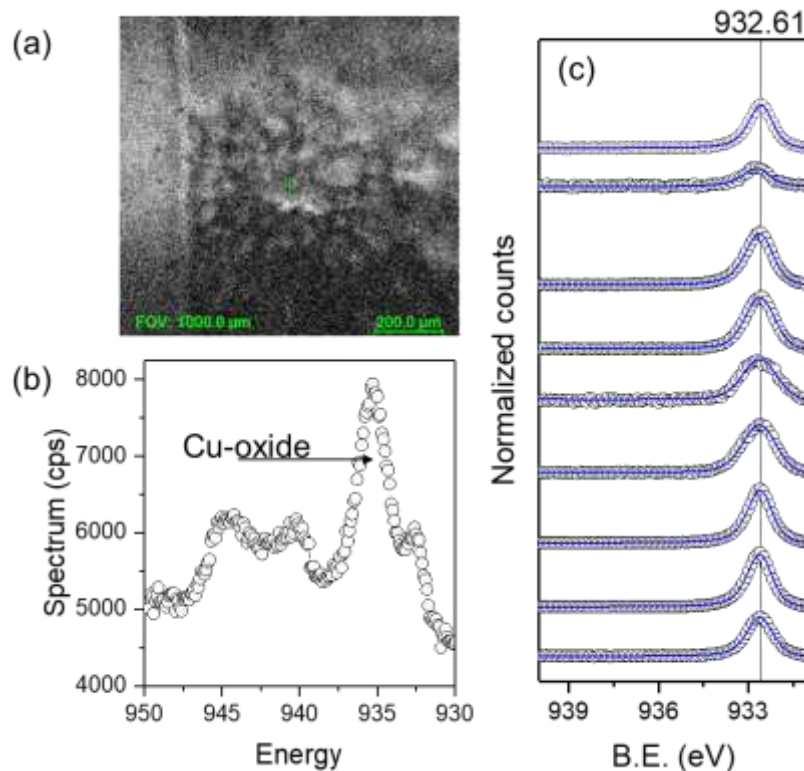


Figure 2.1. (a) SXI image of a Cu-foil with samples on its surroundings, (b) pre-sputtered Cu-foil peak, and (c) sputtered Cu-foil peak

2.4 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) uses a high power x-ray generated by a synchrotron to excite a core electron to an unoccupied orbital above the Fermi level. The energy needed to excite this core electron is reflected in x-ray absorption near edge spectroscopy (XANES) region of XAS. This energy can be correlated with the oxidation state of the materials. Once the core electron is ejected it can interact with other orbitals of the surrounding atoms creating a ripple effect. The ripple effect happens in form of waves and thus constructive interference and destructive interference of these waves give rise to the wave

like signal in the extended x-ray absorption fine structure (EXAFS) region of XAS. Usually, the XAS data is collected using Beer's Law principle (Equation 2.3). The I_0 is the gas coefficient measured inside the inlet gas chamber before the x-ray beam reaches the sample. Meanwhile, the I_t is measured at the outlet gas chamber. Reference materials are usually run with the sample to remove shifts caused by the instrument.

$$\mu_t = \ln\left(\frac{I_0}{I_t}\right) \quad (\text{Equation 2.3})$$

2.5 Transmission electron microscopy

Transmission electron microscope (TEM) works similar to an optical microscope. However, since the light source in TEM is electron with smaller wavelength, it has higher magnification than an optical microscope.

The electron from the electron gun (200-300 keV) is accelerated through an electromagnetic field and passes through the condenser lens whose function is to remove high angle electrons. The electron then goes through the thin samples and is transmitted. The transmitted electron goes through the objective lens and lastly a projector lens projects the images to a screen or camera. This image has a resolution to around 0.2 nm and thus it is sufficient to resolve d-spacing on the crystal planes.

TEM can also be used to observe the diffraction pattern by using an additional diffraction aperture to image the diffracted electrons. Similar to XRD, only the certain planes that constructively interfere would be displayed on the

screen. This diffraction pattern could be indexed to assign planes to the observed pattern. This diffraction technique is advantageous compared to XRD because it can resolve diffraction pattern for really small particles such as in supported samples.

2.6 Scanning electron microscopy

Scanning electron microscope (SEM), like TEM, also uses electron as the light source for imaging. After the electron is focused using a condenser lens, it is converged again using the objective lens before reacting the sample. The main difference between TEM and SEM is the location of sample. In TEM, the sample is located between the condenser and objective lenses, while SEM sample is placed after the objective lens. SEM raster the samples on the selected area. When the electron beam interacts with the sample, secondary electrons and back scattered electrons are generated. The secondary electrons usually come from the surface of the samples. As a result, the detection of the secondary electrons result in the imaging of the sample surface morphology. However, the back scattered electrons come from a deeper level of the sample. Detection of the back scattered electron yield different information compared to the secondary electron detection. Lastly, x-ray can also be produced during the electron-sample interaction. This x-ray energy is usually unique for each element and thus often used in elemental analysis attached to the SEM unit.

2.7 Energy dispersive x-ray spectroscopy

Energy dispersive x-ray spectroscopy (EDS or EDAX) are often attached to a TEM or SEM unit to measure the elemental composition of the area of interest. When the electron beam interacts with the sample, some of the core electron from the sample is ejected. Consequently, the electron from the outer shell with higher energy fills in the hole of the core electron, releasing energy in the process in the form of x-ray. The energy is captured by an EDS detector and this energy is distinct for each element, making quantification of elemental composition possible. Since the EDS is attached to an TEM and SEM, the elemental composition is highly dependent on the area of analysis and not representative of the bulk sample. For this reason, EDS elemental composition is categorized as surface characterization.

2.8 Inductively coupled plasma – optical electron spectroscopy

Bulk elemental composition is done with inductively coupled plasma – optical electron spectroscopy (ICP-OES). The samples are first diluted in aqueous media. Typically, metal-based catalysts are diluted in acidic media (~2-5 wt%) to lower than 100 ppm metal contents. Some metals such as Ru does not dissolve in acid. Therefore, other media such as concentrated NaOCl is used.

The ICP chamber is used to create plasma from a gas (i.e., Ar) flowing through a “torch” or intense electromagnetic field generated from radio frequency coil. The diluted sample is introduced to a sample using a pump and a nebulizer to turn the liquid sample into mist. When the mist reaches the plasma chamber,

the samples are constantly ionized due to a high temperature (~7000K). The collision between the plasma and the samples results in the excitation and relaxation of electrons. The relaxation process yields energy in wavelengths specific to the element. The OES chamber then separates these wavelengths and quantifies their peak intensities. External calibration is used to then translate these intensities into concentrations.

2.9 Diffuse reflectance infrared Fourier transform spectroscopy

Infrared spectroscopy (IR) uses IR beam at different wavelength to measure the amount of light absorbed or transmitted by the sample. The absorption wavelength is characteristic of certain bond vibration frequency. This technique is used to observe molecular structure either of the material itself or on the surface of the material depending on the background collection.

There are many types of IR cell depending on the beam path. For example, Fourier transform infrared (FTIR) with transmission cell requires a relatively thin samples for the beam to go through the samples. This analysis allows the IR beam to go through the entire samples making this method quantifiable. Other accessories such as diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy shines the IR beam on top of the sample cup resulting in reflection, diffusion, or scattering of the light source. The light is then reflected by a mirror to the detector. The data obtained from the DRIFT set up is not quantifiable. However, the method still provides information about chemical structures. The work in the thesis takes advantage of the DRIFT spectroscopy to

analyze surface interaction with adsorbates such as pyridine to yield information about the surface acidity.

2.10 Chemisorption

The chemisorption of the molecules on the catalyst surface involves a formation of a chemical bond between the adsorbates and the catalyst surface. This process usually releases an energy of 20-400 kJ/mol.² The chemisorption unit is equipped with thermal conductivity detector (TCD) that reacts to changes in gasses. Pretreatment methods to remove water and remove surface oxidation are employed pre-analysis. Some of the experiments performed in this thesis involves using chemisorption unit to quantify the active sites of the materials. Probe adsorbates like CO can bind to electron deficient sites. The assumption such as one CO molecule binds to one active site is made. Since CO binds strongly to the catalyst surface, the CO adsorption is usually done with a pulse experiment at low temperature (35°C). Other probe molecule such as NH₃ can also be used to quantify the acid sites on the material. Unlike CO, NH₃ can desorb from the catalyst surface at below 400°C. A typical experiment from NH₃ chemisorption involves a temperature programmed desorption (TPD) experiment where the surface is saturated with NH₃ and slowly desorbed at a controlled temperature ramp rate. Multiple features such as weakly and strongly adsorbed acid are usually observed at low and high desorption temperature respectively.

2.11 N₂ physisorption

N₂ physisorption is used to measure textural properties of the material such as surface area, pore volume, and pore size. Unlike the chemisorption, physisorption involves mild interaction (van der Waals) of the adsorbate and the solid surface. The adsorption energy is usually low at 10-40 kJ/mol.²

In a physisorption experiment, it is important to pretreat the sample under vacuum and heat to remove any physically adsorbed species. The N₂ adsorption is done under vacuum and in liquid N₂ (77 K) by dosing small amounts of N₂ and measuring the equilibrium pressure. The desorption curve is obtained by slowly degassing the system and measuring the pressure/volume of gas desorbed. The adsorption and desorption curve are used to measure the textural properties. The shape of the curve can quantitatively give information about the pore sizes of the samples.

Multiple analysis can be applied to the adsorption and desorption curve. One of the most common analysis is the Brunnauer-Emmett-Teller (BET) theory.³ This theory is applicable to some types of materials such as non-porous/microporous solid (type II) and mesoporous solid (type IV). The BET theory assumes that one molecule adsorbs on one site. However, these adsorbed molecules can act as adsorption site for the next layer. The topmost layer is assumed to be at equilibrium with the gas environment.

$$\frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C} \frac{p}{p_0} \quad (\text{Equation 2.4})$$

The BET equation (Equation 2.4) is used to calculate the amount of N₂ adsorbed on the surface where p₀ is saturation pressure, p is the measured equilibrium pressure, V is the volume of adsorbed gas, V_m is the volume of adsorbed monolayer, and C is the BET constant. The plot of p/(V(p₀-p)) vs. p/p₀ gives a slope and intercept that can be used to calculate C and V_m. The surface area can then be calculated with Equation 2.5 where N is Avogadro number and m is the mass of the sample.

$$S_{BET} = \frac{V_m N}{m} \quad (\text{Equation 2.5})$$

2.12 Gas chromatograph mass spectrometer

The gas chromatograph (GC) mass spectrometer (MS) combines the separation ability of the GC and the robust quantification method of the MS to achieve quantification of organic molecules. Liquid (or gas) samples are injected into the GC column. The separation occurs due to different interaction between the organic molecules and the stationary phase (i.e., coating materials of the GC column) as it is being pushed through the column by the mobile phase (i.e., inert carrier gas such as He). The column is heated to keep molecules with higher molecular weight in the gas phase. Molecules with weak interaction with the column elute faster and exit the column at a lower retention time.

After the molecules are separated, they enter the MS chamber where a filament is used to ionize the molecules. Due to the high energy imparted on the molecules, the molecules start to fragment. These fragments are captured by a

mass analyzer in the form of mass to charge (m/z) ratio. This fragmentation pattern is unique and thus a fingerprint of different molecules. Through the fragmentation pattern, the molecules can be identified from a database and the m/z ratio can be used to quantify the concentration of the molecules with external calibrations.

2.13 References

1. Bragg, W. H.; Bragg, W. L., The reflection of X-rays by crystals. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **1913**, 88 (605), 428-438.
2. Králik, M., Adsorption, chemisorption, and catalysis. *Chemical Papers* **2014**, 68 (12), 1625-1638.
3. Brunauer, S.; Emmett, P. H.; Teller, E., Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, 60 (2), 309-319.

CHAPTER 3

PERIODIC TRENDS FROM METAL SUBSTITUTION IN BIMETALLIC MO-BASED PHOSPHIDES FOR HYDRODEOXYGENATION AND HYDROGENATION REACTIONS[†]

3.1 Introduction

As explained in the introduction, the discovery of new catalysts for the selective hydrodeoxygenation (HDO) of biomass-derived compounds is an important step towards the valorization of biomass due to the high complexity of lignocellulosic biomass.

Multifunctionality is important in catalytic HDO reactions because the catalyst is required to carry out multiple reactions: dissociative adsorption of H₂ and C-O cleavage via hydrogenolysis.^{3, 8} The synthesis of supported bimetallics can be tailored to yield catalysts with bifunctional sites. As an example, hydrogenating metals (Pt, Pd, Ru, Ni) split H₂, while oxophilic metals (Re, Mo, W, Fe) bind to the hydroxyl group in a mixed supported metals system.^{3, 9} In other

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materials such as sulfides and oxides, multifunctionality exists as 1) a surface vacancy that could be filled with the O atom from the hydroxyl functionality and 2) proton donors (e.g., S-H in sulfides or O-H in carbides).¹⁰ Metal phosphides are also well suited for HDO reactions due to their multifunctional nature, which also results in the ability to catalyze a variety of other reactions pertaining to biomass upgrading. In our previous work, we showcased the multifunctionality of FeMoP for both the HDO of phenol and the acid-catalyzed dehydration of cyclohexanol.¹¹ FeMoP catalyzed the dehydration of cyclohexanol to cyclohexene in the absence of H₂ using the presence of surface acid sites (i.e., Lewis and Brønsted) to promote the reaction.¹¹ Moreover, in the presence of H₂, FeMoP was able to perform HDO of phenol, with selectivities >90 % at significantly higher H₂ pressures than often studied (750 psig).¹¹ The presence of these sites and their respective roles in HDO have also been confirmed by other works using NiMoP and Ni₂P.¹²⁻¹⁴

Although this article is focused on metal phosphides, other notable materials such as supported metals,²⁴⁻²⁶ metal sulfides,²⁷⁻³⁰ metal oxides,³¹⁻³³ and metal carbides³⁴⁻³⁶ have also been studied for HDO reactions.

Because most metals in the periodic table can form solid solutions of metallic and bimetallic phosphides in a variety of crystal structures, the multifunctionality of these materials can be directly controlled with the choice of metal(s).²⁰ Further tuning of the catalytic properties is available by altering the ratio between metal(s) and phosphorus while maintaining the bulk structure. For example, we altered the ratio between Fe:Mo in orthorhombic FeMoP and

tracked the change in the lattice parameters as a function of metal composition.³⁷ As catalysts, the Fe:Mo ratio significantly influenced the selectivity of the products for phenol HDO due to the resulting charge transfer between the metals and phosphorus atoms, which caused an electronic effect that was observed in the reaction products.³⁷ Chen et al. performed a similar study by varying the composition of $\text{Ni}_x\text{Mo}_y\text{P}/\text{SiO}_2$ and found the addition of Ni decreased the acidity and limited the selectivity to C-O bond cleavage.³⁸ The effects on reaction selectivity due to the metal(s) and phosphorus composition have also been observed by Oyama and co-workers in FeNiP and is another example of optimizing metal phosphides for selective transformations.³⁹

Although the highlighted works show extensive studies on catalytic consequences of changing metals to phosphorus ratios, the effect of metal type has not been thoroughly explored. To elucidate this effect, a series of Mo-based bimetallic phosphides were used because MoP provided a higher selectivity towards deoxygenated product in anisole HDO compared to FeP.²¹ The same effect has also been reported in another study comparing MoP and Ni_2P .¹³ In this work, we report the synthesis and detailed characterization of Mo-based bimetallic phosphides MMoP ($M = \text{Fe}, \text{Co}, \text{Ni}$) and correlate the relative oxidation of Mo to the benzene selectivity in phenol HDO. To obtain a defined bulk crystal structure to ensure the formation of bimetallic phosphides, unsupported materials were synthesized. Additionally, Ru was also included in this study to observe similarities and differences in the performance of Group 8 incorporated bimetallic catalysts (FeMoP vs. RuMoP). The materials were then tested as HDO catalysts

at both high temperature (400°C) and low temperature (125°C) in the liquid phase to demonstrate the versatile applications of these catalysts. Finally, cascade reactions were performed using a combination of bimetallic phosphides to further showcase the control in the HDO product distribution.

3.2 Experimental

3.2.1 Materials

All chemicals were used as received: $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 99%), $(\text{NH}_4)_2\text{HPO}_4$ (Amresco, 98%), $\text{FeNO}_3\cdot 9\text{H}_2\text{O}$ (Alfa Aesar, 99%), $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99%), $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99%), RuCl_3 hydrate (Alfa Aesar, 99%), citric acid (Alfa Aesar, 99%), phenol (Sigma-Aldrich, 99%), cyclohexanol (Alfa Aesar, 99%), cyclohexanone, benzene (Alfa Aesar, 99%), cyclohexene (Alfa Aesar, 99%), cyclohexane (Acros Organics, 99%) decane (Alfa Aesar, 99%), and Davisil® silica gel (Sigma Aldrich, Grade 635, 60-100m). All gas cylinders (purity of $\geq 99.995\%$) were purchased from Airgas: Ar, He, N_2 , H_2 , 1 % O_2/He , 30 % CO/He , and 2 % NH_3/He .

3.2.2 Material synthesis

Unsupported bimetallic phosphide catalysts were synthesized through a standard temperature programmed reduction (TPR) method. In a typical synthesis, citric acid was dissolved in deionized water followed by addition of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, the *M* precursor ($\text{FeNO}_3\cdot 9\text{H}_2\text{O}$ for Fe, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ for Co, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ for Ni, or RuCl_3 hydrate for Ru) and $(\text{NH}_4)_2\text{HPO}_4$, respectively. The mole ratio between the citric acid to metals (*M* + Mo) was

adjusted to 0.7, while the other precursors were added in 1:1:1 ratio of *M*:Mo:P to form 0.1 mol Mo/L aqueous solution. Note: In the synthesis of NiMoP and RuMoP, excess citric acid caused phase impurities where monometallic phases were observed in the diffraction patterns. Therefore, optimization of the citric acid is important in controlling the phase purity of the metal phosphide. The solution was stirred for an hour, and subsequently, the liquid volume was reduced by 1/2 using a rotary evaporator. The concentrated solution was then dried at 200°C for 2 hr using a 1°C/min ramp rate. The resulting brown material was ground to a powder and calcined at 550°C for 6 hr using a ramp rate of 1°C/min. The powders were subsequently reduced in a Lindberg Blue M tube furnace using 160 mL/min of H₂ at 100°C for 1 hr, 260°C for 1 hr, and 650°C for 2 hr using a 5°C/min ramp rate to reach each set point. Lastly, the resulting pyrophoric powders were passivated with 160 ml/min of 1% O₂ in He at room temperature for an hour. After passivation, all materials were stored in a N₂ glove box.

3.2.3 Material characterization

The crystal structures of the materials were characterized using a Bruker DaVinci Advanced D8 powder X-ray Diffractometer (XRD) with a CuK α radiation source from 20°-60° 2 θ . The Brunauer-Emmett-Teller (BET) surface area was obtained using a Quantachrome Nova 2200e physisorption unit with 24 h degas time at 150°C. The number of CO accessible sites and acid sites were quantified using a Micromeritics Chemisorb 2750. For both analyses, the sample was

pretreated at 400°C under H₂ for 2 hr to prevent and/or minimize polycarbonyl formation followed by flowing He at 30 mL/min for 1 hr at the same temperature. The number of CO accessible sites was determined by pulse chemisorption with a 30% CO in He gas mixture at 35°C. The area obtained from the thermal conductivity detector (TCD) signal was correlated to the moles of CO fed via a calibration curve. The number of total acid sites was measured using NH₃-temperature programmed desorption (TPD). NH₃ was chemisorbed to the catalyst at 100°C for 2 hr and desorbed at a ramp rate of 10°C/min with a 42 minutes isothermal step at both 230°C and 400°C. The peak areas were quantified with an external calibration curve to relate the NH₃ loading to the amount of acid sites on the catalysts.

Elemental analysis was performed using a Perkin Elmer Optima 8000 inductively coupled plasma optical emission spectrometer (ICP-OES). The sample was diluted to 1-50 ppm for each element for analysis and fitted to an external calibration curve for each element. A JEOL 3011 transmission electron microscope (TEM) was used to collect the TEM images and to perform energy dispersive x-ray (EDX) spectroscopy. The samples were deposited on the electron microscopy HC200-CU-100 grid by drop casting using acetone as the solvent. The samples were dried under vacuum for an hour prior to analysis.

X-ray photoelectronic spectroscopy (XPS) was utilized with a PHI VersaProbe II to characterize the surface of the materials. The samples were prepared in the glovebox and quickly transferred to the XPS transfer arm with minimum exposure to air to prevent additional surface oxidation and moisture

contamination. The resulting XP spectra were processed using SmartSoft-VersaProbe software. For reference, the binding energy for the C peak was shifted to 284.8 eV. The P 2*p* region was deconvoluted to reduced P 2*p*_{3/2} and P 2*p*_{1/2} regions. Meanwhile the satellite peak at the higher binding energy was deconvoluted to P 2*p*_{3/2} and the P 2*p*_{1/2} and was attributed to cationic P as suggested by others.⁴⁰⁻⁴¹ Similarly, the Mo 3*d* region was also deconvoluted to reduced Mo 3*d*_{5/2} and Mo 3*d*_{3/2}. The satellite peak at higher binding energies was assigned to oxidized Mo 3*d*_{5/2} and Mo 3*d*_{3/2}. It is possible that the cationic P and Mo species could form during passivation or during brief exposure to air during sample transfer to the XPS chamber. X-ray absorption spectroscopy (XAS) was performed at Argonne National Laboratory at the Advanced Photon Source (APS) sector 10 Insertion Device (ID) beam-line of the Material Research Collaborative Access Team (MRCAT). Samples were diluted in boron nitride and pressed into a wafer in a six-shooter placed in an air-tight pretreatment cell. They were pretreated at 400°C under 4% H₂ in He for an hour before analysis. The experiment was run under transmission mode with a 10⁵ photon flux per second. The data analysis was performed using WinXAS version 3.1 software.

3.2.4 Catalytic testing

The catalytic performance of the synthesized bimetallic phosphides was tested in an up-flow stainless steel flow reactor equipped with 10 μm stainless steel mesh to hold the catalyst in place. In a typical experiment, the catalyst bed was packed with 50 mg 60-100 mesh Davisil® silica followed by 30 mg 150 μm –

250 μm pelletized catalyst diluted in 120 mg silica, 25 mg silica gel, and finally 10 mg quartz wool. Catalyst pretreatment was accomplished in a stream of flowing H_2 at 400°C for 1 hr with a gas flow rate of 100 mL/min. After catalyst pretreatment, the reactor was pressurized to 750 psig with H_2 , and decane was subsequently pumped at 1 mL/min using a Hitachi L-6000 HPLC pump. The temperature was controlled using a PID controller to the desired temperature. Once the temperature was stable, the feed solution was switched to 0.13 M phenol in decane. The concentration of the remaining reactants and products in the liquid samples were quantified using an Agilent gas chromatograph 7890/mass spectrometer 5975 (GCMS) with external calibration for reactants and products. The cascade experiment in the batch reactor was performed in a 250 mL Parr pressure vessel. Approximately 30 mL of the liquid feed was loaded into the reactor. Before the experiment, the vessel was purged three times with 450 psig N_2 , then with 450 psig H_2 before being charged with 400 psig H_2 . After the reaction, the reactor was cooled to room temperature before the liquid sample was quantified with GCMS. The selectivity and conversion were calculated with equation 1 and 2 below.

$$\text{Selectivity} = \frac{n_{\text{desired product}}}{\sum n_{\text{products}}} \quad (1)$$

$$\text{Conversion} = 1 - \frac{n_{\text{Phenol,out}}}{n_{\text{Phenol,in}}} \quad (2)$$

3.3 Result and discussion

3.3.1 Catalyst synthesis and characterization

Various Mo-based bimetallic phosphides $MMoP$ were synthesized using elemental combinations across the first-row transition metal M (Fe, Ni, Co; Ru for comparison to Fe) by temperature programmed reduction (TPR). The choice in M was based on the reported performance of the bimetallic catalysts MMo in other works for heteroatom removal.^{21, 42-44} Fe was chosen because $FeMoP$ has shown remarkable performance as HDO catalyst.²¹ Meanwhile, sulfided NiMo and CoMo supported on Al_2O_3 are the industrial catalyst for heteroatom removal in hydrotreating, and thus these metal combinations were of interest.⁴²⁻⁴³ In addition, previous reports have shown sulfided $RuMo/Al_2O_3$ showed a higher deoxygenation selectivity to benzene and cyclohexane during HDO of diphenyl ether in comparison to its aromatic hydrogenation ability tested for naphthalene hydrogenation to tetralin.⁴⁴ Although a range of compositions of $M:Mo:P$ produce solid solutions, not all metal combinations span the same compositional range. Therefore, the 1:1:1 ratio was chosen because all of the materials studied here form known solid solutions. Moreover, our previous study showed that for different Fe:Mo ratios in $Fe_xMo_yP_z$, the highest selectivity to benzene (90%) from phenol was achieved using $Fe_xMo_yP_z$ close to 1:1:1 ratio.²¹

All the materials were analyzed with XRD to confirm their bulk crystal structures. Figure 3.1 shows the diffraction patterns of the synthesized materials and the simulated reference patterns for $RuMoP$, $NiMoP$, $CoMoP$, and $FeMoP$, respectively. The three most intense peaks were identified for each of the

bimetallic structures and marked with black stars for orthorhombic (FeMoP, CoMoP, RuMoP) and green circles for hexagonal (NiMoP) crystals. The crystal structures of $MMoP$ ($M = \text{Fe, Co, Ni, Ru}$) are presented in Figure A.1. FeMoP, CoMoP, and RuMoP have the same space group (Pnma) and MnP-type structure, while NiMoP (P62m) follows Fe_2P -type structure. The crystal information was summarized in Table A.1. In contrast with nitrides and carbides and similar to borides, silicides, and sulfides, the metal atoms in phosphides typically follow a triangular prismatic arrangement where the metal atoms surround a central phosphorus atom.⁴⁵⁻⁴⁶ The two types of sites that have been suggested in Ni_2P and FeNiP are tetrahedral and square pyramidal coordination sites.⁴⁷ The tetrahedral site has been correlated with direct heteroatom removal, while the square pyramidal site has been shown to influence the hydrogenation activity. Other studies have shown that metal siting depends on the composition, such as in $\text{Fe}_x\text{Ni}_{2-x}\text{P}$ where Fe occupies the square pyramidal site when $x > 0.6$ and otherwise the tetrahedral site.⁴⁸

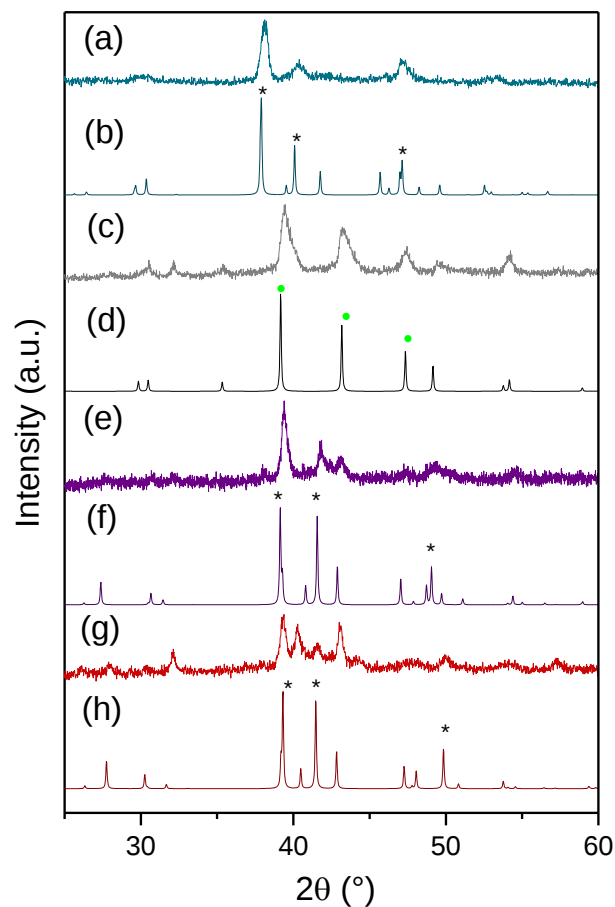


Figure 3.1. Powder XRD patterns of (a) RuMoP (b) reference pattern for RuMoP (PDF 04-015-7732) (c) NiMoP (d) reference pattern for NiMoP (PDF 00-031-0873) (e) CoMoP (f) reference pattern for CoMoP (PDF 01-071-0478) (g) FeMoP (h) reference pattern for FeMoP (PDF 04-001-4637).

The three most dominant peaks in FeMoP and RuMoP are (112), (211), and (020), respectively. Meanwhile, the three most dominant peaks in NiMoP are (111), (201), and (210), respectively. High resolution TEM (HRTEM) images were obtained to further confirm the crystallinity of the materials (Figure 3.2). Figure 3.2d shows the HRTEM images of RuMoP with the (112) plane and (211) plane, which are the two most dominate planes in the RuMoP pattern. The dominant plane (112) is also observed in the TEM images of FeMoP and CoMoP (Figure

3.2a and 3.2b). Meanwhile the (111) plane is observed in NiMoP HRTEM, which is also the dominant plane observed through XRD.

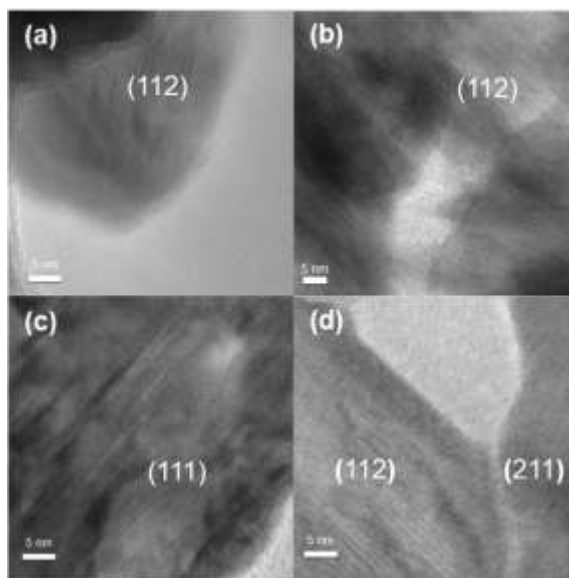


Figure 3.2. HRTEM images of (a) FeMoP (b) CoMoP (c) NiMoP and (d) RuMoP.

The textural properties were characterized by multiple methods, and the results are summarized in Table 3.1. The BET surface areas ranged between 6-12 m²/g, which was similar to other works on unsupported transition metal phosphides.^{11, 21, 49} The acid site densities were probed using NH₃ TPD, which resulted in two distinct peaks at ~210°C and ~320°C for each of the materials. The peak at around 210°C was correlated with the presence of Brønsted acidity from surface P-OH groups, while the peak at 320°C was attributed to the desorption of NH₃ from Lewis acid metal sites (M^{δ+}).¹³ The acidity, ρ_{acid} , is reported as the total acidity per gram representing the total peak areas obtained from the two regions of the NH₃ TPD (Table 3.1). The material with the highest

acid density is RuMoP followed by NiMoP, FeMoP, and CoMoP, respectively. As suggested by previous studies, CO can interact with $M^{\delta+}$ sites and P sites (forming $P=C=O$ species), or it can participate in polycarbonyl formation.⁵⁰ However, surface polycarbonyl formation is unlikely due to our pretreatment condition. Based on the CO-titration data in Table 3.1, RuMoP has the lowest number of N_{CO} relative to other catalysts, while FeMoP, CoMoP, and NiMoP have similar values for N_{CO} . The bulk material composition was obtained through ICP- OES and shows that the M:Mo:P ratio were very close to 1:1:1 target ratio for all synthesized materials.

The surface properties were also investigated using XPS (Figure 3.3). In Figure 3.3(a) and 3.3(b), the XP spectra of the P 2*p* region and Mo 3*d* region were plotted for FeMoP, CoMoP, NiMoP, and RuMoP from top to bottom respectively. The peaks were deconvoluted based on the reduced (blue and green) and oxidized (magenta) species described in experimental section.⁵¹⁻⁵⁴

In FeMoP, NiMoP, and CoMoP, the position of the P 2*p*_{3/2} binding energy shift is 129.33 eV, 129.60 eV, and 129.66 eV, respectively, while the binding energy shift for RuMoP is higher at 130.31 eV (Figure 3.3a). The highest reported P 2*p*_{3/2} binding energy shift for P with oxidation state of 0 was reported at 130.9 eV.⁵⁵ This value is higher compared to the P in bimetallic phosphides, indicating the oxidation state of the P in all the bimetallic phosphides are slightly anionic.⁵⁵ The measurements agree with other works that have observed lower binding

energies in phosphides in comparison to elemental P due to the charge transfer between the metals and P atoms.⁵⁶

TABLE 3.1.
TEXTURAL PROPERTIES AND ELEMENTAL ANALYSIS.

Catalysts	S_{BET}	N_{Co}	ρ_{acid}	Elemental analysis (ICP)		
	(m^2/g)	($\mu\text{mol/g}$)	($\mu\text{mol/g}$)	M	Mo	P
FeMoP	12	30	27	1.00	0.99	1.00
CoMoP	7.9	26	18	1.00	1.00	1.00
NiMoP	7.6	31	30	1.00	1.00	1.00
RuMoP	6.8	18	53	1.01	1.00	1.00

The Mo 3d region was deconvoluted based on the method described in experimental section. The Mo 3d_{5/2} binding energy shifts are 227.74 eV, 227.68 eV, and 227.62 eV for FeMoP, CoMoP, and NiMoP, respectively, while the binding energy shift of Mo 3d_{5/2} in RuMoP is 228.58 eV (Figure 3.3b). Compared to the elemental Mo⁰ reference (B.E. 226.67 eV), the Mo in the bimetallic phosphides is slightly oxidized. These observations were also reported in several other literatures that showed partially oxidized Mo metal in MoP.^{41, 57} However, a formal oxidation state was not assigned due to the asymmetric lineshape observed in XP spectra

for phosphides, which arises due to the excitation and scattering of valence electrons interacting with the core hole.⁵⁸ The satellite peak or the tail in the spectra instead of distinct peaks makes it difficult for precise deconvolution, and qualitative assessment is sufficient for comparison between materials.⁵³

Since the binding energy shifts depend on the charge transfer between metal-metal and metals-P interactions, we correlated the binding energy shifts with the electronegativity, which represents the atomic charge properties. Mar and co-workers have exploited this relationship by showing a strong linear correlation between the difference in electronegativity in phosphides with the binding energy shift in P $2p_{3/2}$ region.⁵³ For bimetallic phosphides, metal-metal interactions must also be considered when determining the difference in electronegativity in addition to metals to P interactions. Therefore, Equation 3 was derived and used to calculate the electronegativity difference in the bimetallic phosphides studied herein, where χ describes the electronegativity for phosphorous (P), the first metal (M') and the more electronegative second metal (M).

$$\Delta\chi = \chi_P - \left[\frac{(2-x)}{2} \chi_M + \frac{x}{2} \chi_{M'} \right] + \frac{(2-x)}{3} (\chi_M - \chi_{M'}) \quad (\text{Equation 3.3})$$

Because there are various electronegativity scales, we examined three different scales for comparison: Allred-Rochow, Pauling, and Mulliken. The Allred-Rochow electronegativity scale takes advantage of the atomic properties and thus relates to the surface property and binding energy.^{53, 59} The two other

electronegativity scales, Pauling and Mulliken, are both derived based on the thermodynamics and were investigated for consistency. The electronegativities used for the calculations are detailed in Table A.2.

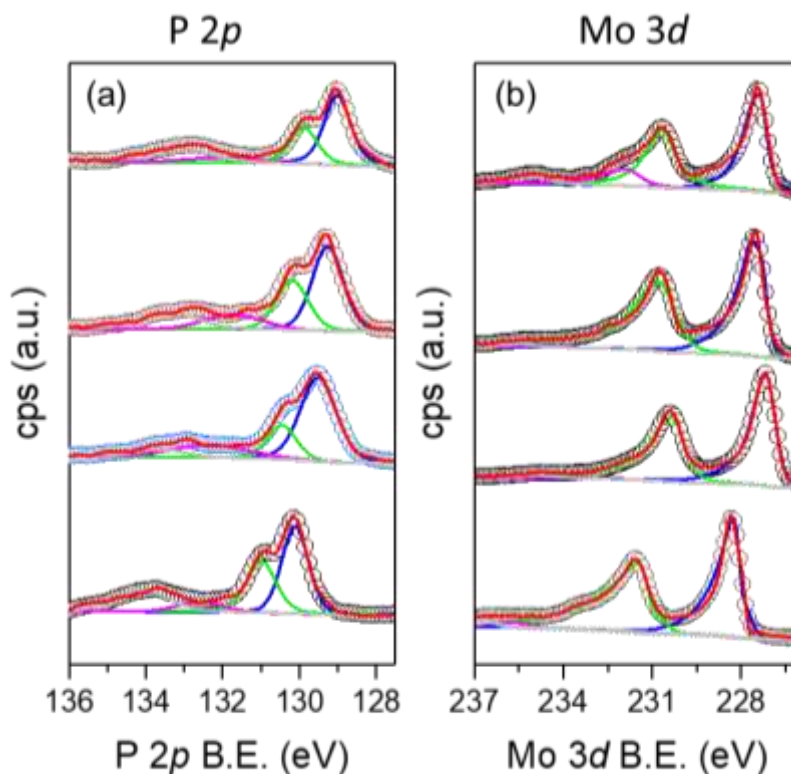


Figure 3.3. XP Spectra in (a) P 2p region and (b) Mo 3d region of (from top to bottom) FeMoP, CoMoP, NiMoP, RuMoP. Empty circle is the raw data, blue line is the reduced P 2p_{3/2} and Mo 3d_{5/2}, green line is reduced P 2p_{1/2} and Mo 3d_{3/2}, magenta line is the oxidized species in P 2p_{3/2} and Mo 3d_{5/2}, gray line is the oxidized species in P 2p_{1/2} and Mo 3d_{3/2}, and red line is the fit of the deconvoluted peaks. All spectra were shifted based on the C reference peak at 284.8 eV.

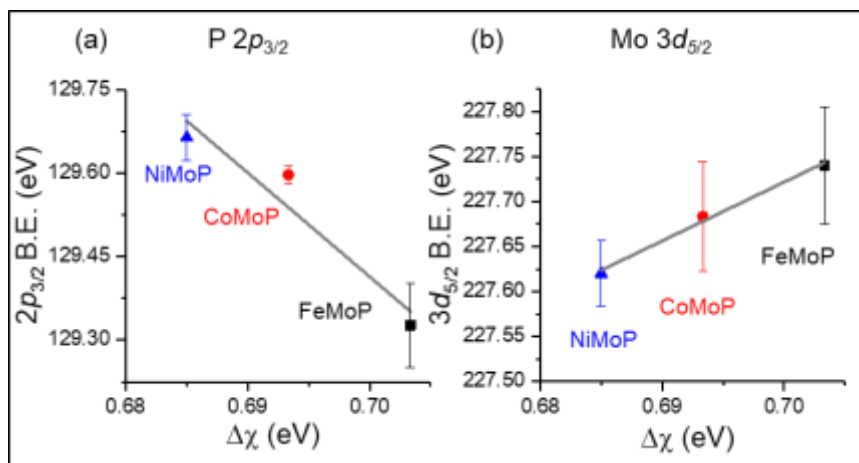


Figure 3.4. The relationship between the electronegativity difference calculated using the Allred-Rochow electronegativity scale and binding energy of (a) P $2p_{3/2}$ and (b) Mo $3d_{5/2}$ for NiMoP (blue triangle), CoMoP (red circle), and FeMoP (black square).

The three electronegativity scales were explored and used to calculate $\Delta\chi$ using Equation 3, which was then plotted with respect to the B.E. shift in the P $2p_{3/2}$ and Mo $3d_{5/2}$ region for $MMoP$ ($M = \text{Fe, Co, Ni}$). Figure 3.4a and 3.4b are plotted based on Allred-Rochow electronegativity scale difference. The binding energy shift in P $2p_{3/2}$ region were linearly correlated with the $\Delta\chi$, which agrees with the work previously described by Mar and co-workers.⁵³ Additionally, our findings show that the shift in B.E. from the Mo $3d_{5/2}$ region also vary linearly with $\Delta\chi$. The linear trends are also observed when $\Delta\chi$ is calculated using the Pauling and Mulliken electronegativity scales, although the slopes are different (Figure A.2). As explained before, the trend was obtained due to the charge transfer between P and the metals causing P to be more anionic when $\Delta\chi$ is larger and conversely, the Mo atom is more oxidized. From these results, the Mo in FeMoP is the most oxidized followed by CoMoP and NiMoP.

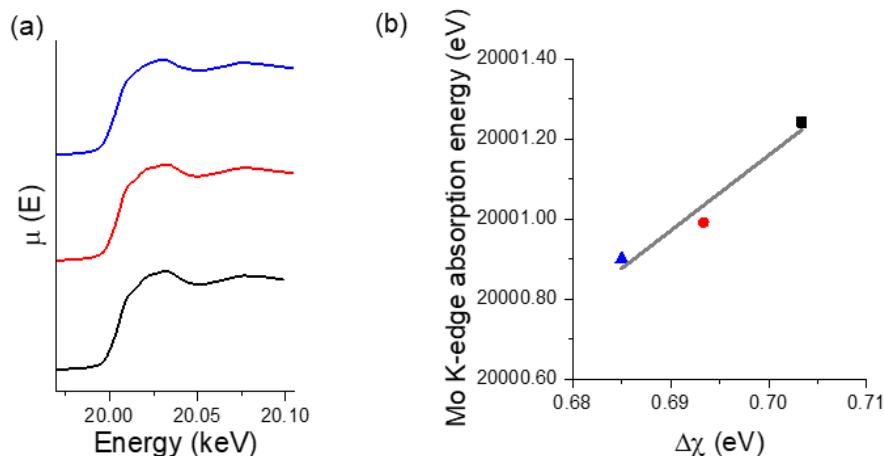


Figure 3.5. (a) Normalized XANES and (b) Absorption energy shifts in the Mo K-edge energy for NiMoP (blue triangle), CoMoP (red triangle), and FeMoP (black square) (a) Normalized XANES and (b) Absorption energy shift in the Mo K-edge energy for NiMoP (blue triangle), CoMoP (red triangle), and FeMoP (black square).

Although the linear trend was observed between the binding energy shift in XPS and $\Delta\chi$, the error bars in Mo $3d_{5/2}$ overlapped. To ensure that the trend was correct, the bulk oxidation state was examined using XANES at the Advanced Photon Source at Argonne National Laboratory. The shift in absorption energy was extracted from the Mo K-edge region of the XANES spectra (Figure 3.5a). Each of the samples was run with a reference Mo foil that was shifted to 20,000 eV for all samples to eliminate external factors. The position of the sharp absorption edge was used for comparison for the spectra and plotted in Figure 3.5 for NiMoP (blue triangle), CoMoP (red circle), and FeMoP (black square). The XANES results show a similar linear trend as observed in XPS. In both cases, the Mo atom in NiMoP is the least oxidized followed by CoMoP and

FeMoP, respectively. To transition from Mo^0 to Mo^{1+} , the shift in absorption energy is ~ 6 eV.⁶⁰ However, the shifts in bimetallic phosphides are only ~ 1 eV, which indicates that the Mo in each of the bimetallic phosphides is slightly positive.

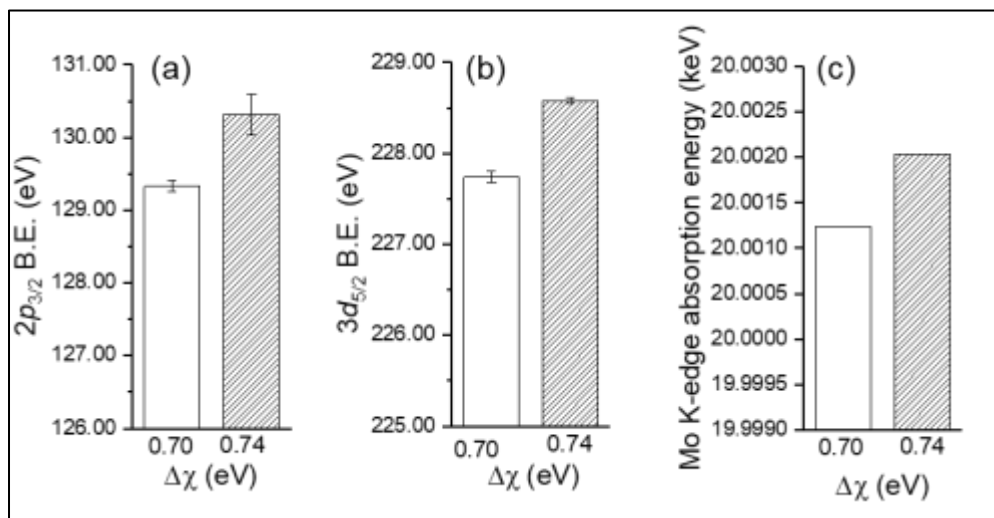


Figure 3.6. The relationship between electronegativity and binding energy of (a) P $2p_{3/2}$ and (b) Mo $3d_{5/2}$ determined by XPS and (c) the absorption energy shift determined by Mo K-edge XANES for FeMoP (empty bar) and RuMoP (shaded bar) using Allred-Rochow electronegativity scale.

A similar comparison was also done for FeMoP and RuMoP using XPS (Figure 3.6a-b) and XANES (Figure 3.6c). Both the binding energy of the P $2p_{3/2}$ and Mo $3d_{5/2}$ regions increase from FeMoP to RuMoP unlike the previous results for the other three bimetallic phosphides across the periodic table. The binding energy in the P $2p_{3/2}$ region shifts from 129.33 eV to 130.31 eV, while the shift in Mo $3d_{5/2}$ was observed from 227.74 eV to 228.57 eV for FeMoP and RuMoP, respectively. The P in RuMoP is more oxidized than the P in FeMoP due to less charge transfer between P and the two metals because the electronegativity of

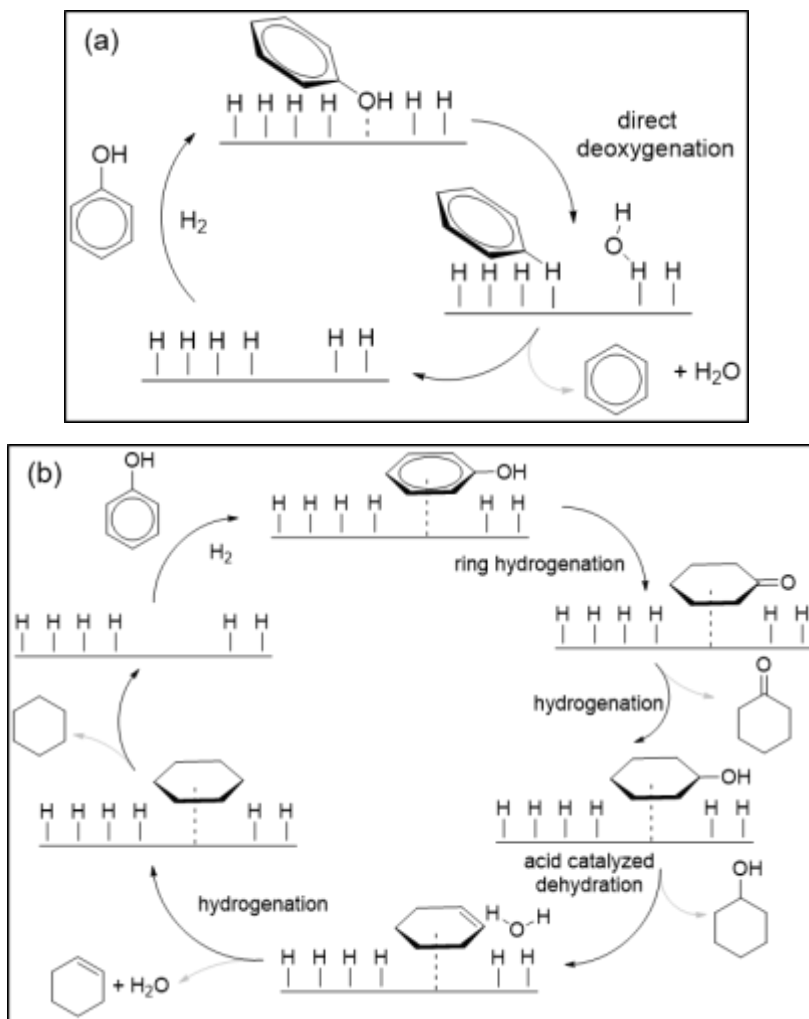
Ru (1.42) and Mo (1.3) is closer than Fe (1.64) and Mo. In Figure 3.6c, the absorption energy shift measured by XANES was plotted against $\Delta\chi$ calculated using the Allred-Rochow electronegativity scale. The trend in both XPS and XANES was again in agreement with one another, where the Mo in RuMoP is more oxidized compared to FeMoP.

3.3.2 Catalyst performance

The relative oxidation of the metals in bimetallic phosphides has a direct effect on the interaction with the O atom in phenol for HDO, as we previously observed with FeMoP where phenol preferentially binds to the slightly positive Fe and Mo.³⁷ Herein, the the degree of oxidation of the Mo in MMoP was also studied using phenol HDO, which was a good probe reaction due to the reaction pathways possible (Scheme 3.1): direct deoxygenation (DDO, Scheme 3.1a) and hydrogenation (HYD, Scheme 3.1b).

From computational studies, the hydroxyl group interaction with the phosphide occurs by the aromatic ring orienting either coplanar (parallel) or nonplanar (titled) with respect to the surface.⁸ Coplanar orientation drives the selectivity to hydrogenated products (HYD) due to the proximity of the ring to the H species on the catalyst surface, while a nonplanar orientation leads to the direct deoxygenation product (DDO). The adsorbates' orientations can be influenced by the surface properties such as surface electronics (expressed as Lewis acidity³⁷) or oxophilicity as reported in multiple works.^{9, 25, 61} In the case of phenol HDO, the DDO pathway produces benzene (Scheme 3.1a), while the HYD pathway produces cyclohexanone that tautomerizes and hydrogenates into

cyclohexanol followed by dehydration into cyclohexene and further hydrogenation into cyclohexane (Scheme 3.1b).



Scheme 3.1. Reaction pathways of phenol HDO through (a) DDO and (b) HYD with a H-saturated surface.

Phenol HDO was performed in an up-flow reactor at 750 psig and 400°C to test the catalytic activity of the various materials. Figure 3.7 shows the selectivity towards the DDO product plotted with respect to phenol conversion. For each MMoP ($M = \text{Fe, Co, Ni, Ru}$) catalyst, the DDO selectivity is fairly

constant from low phenol conversion (7%) to conversions as high as ~60% due to the inability of the bimetallic phosphides to hydrogenate benzene.¹¹ Across the periodic table, the selectivity towards the DDO product decreases from FeMoP >> CoMoP > NiMoP.

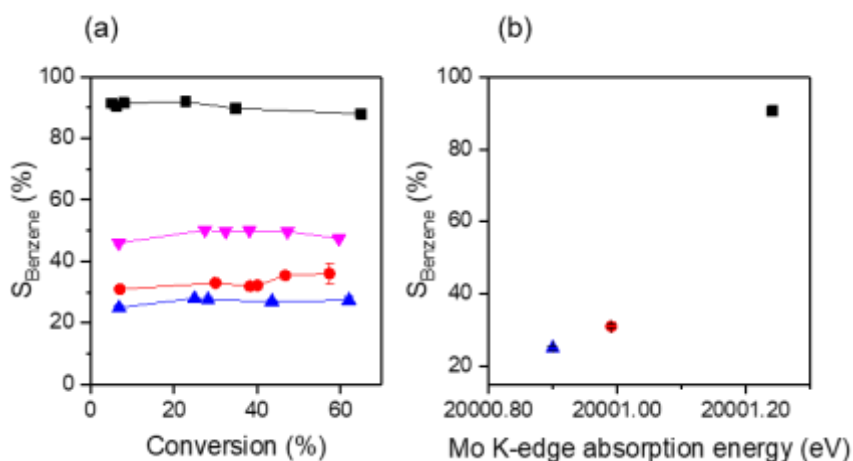


Figure 3.7. (a) Product selectivity 750 psig, 400°C at various conversion using FeMoP (black squares), RuMoP (magenta inverted triangles), CoMoP (red circles), and NiMoP (blue triangles) (b) Selectivity of benzene plotted with respect to Mo K-edge absorption energy.

Additionally, the selectivity trend for the iron group bimetallic phosphides corresponds well with the binding energy measured using XPS and XANES (Figure 3.7b). One of the first steps in the DDO mechanism with FeMoP is the adsorption of phenol onto the Lewis acid sites.³⁷ The next step involves bond elongation of the $C_{\text{aromatics}}-O$ bond that was more significantly observed in the material with stronger Lewis acid character due to the strong interaction between the Lewis acid and the oxygen atom in phenol.³⁷ The Mo atoms in FeMoP have the highest binding energy and are the most oxidized compared to NiMoP and CoMoP. Consequently, the selectivity to DDO is the highest in FeMoP followed

by CoMoP and NiMoP. Conversely, the P atoms in FeMoP are the most reduced and thus exhibit anionic character causing the electron-rich aromatic ring to be repelled by the surface to facilitate DDO. Interestingly, the selectivity trend is not linear to the Mo K-edge absorption energy. A similar non-linear trend was observed by Resasco and co-workers where the selectivity to the DDO product with SiO₂ supported metals increases on more oxophilic metals due to the stronger binding between O in phenol and the supported metal.⁶²

The DDO selectivity of FeMoP and RuMoP at 750 psig and 400°C is 90% and 45%, respectively, when compared at 7% conversion under steady state conditions. From the XPS results in Figure 3.6a, the P in RuMoP is more oxidized compared to FeMoP causing stronger interaction between the P atoms and the aromatic ring. However, since the Mo is also oxidized, the interaction between O in phenol and the surface is also strong. Therefore, due to these interactions, the selectivity is ~45% to DDO. In several works, Ru has been shown as a good ring hydrogenation catalyst for selective aromatics hydrogenation particularly when other functionalities are present.⁶³⁻⁶⁵

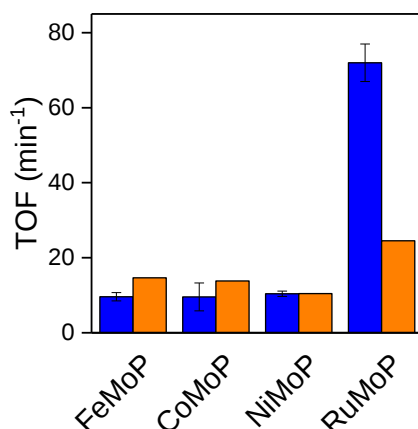


Figure 3.8. TOF of FeMoP, CoMoP, NiMoP, and RuMoP normalized with CO accessible sites (blue) and acid sites (orange).

It is important to note, however, RuMoP is the most active catalyst among all four studied catalysts (Figure 3.8). In a typical experiment, the mass of RuMoP used is four times less compared to FeMoP, CoMoP, and NiMoP to obtain the same conversion. Our previous work showed that the same value for the TOF can be obtained by normalizing the rate in the kinetically limited region with either the acid sites titrated with NH_3 or the CO titrated sites.^{11, 37} Figure 3.8 shows the TOF normalized with CO-accessible sites in blue and the acid sites titrated with NH_3 in orange. To prevent polycarbonyl formation on RuMoP during CO-pulse chemisorption, the sample was pretreated with H_2 .⁶⁶ In this case, the amount of CO-titrated site was within the same value compared to materials pretreated with H_2 and heated under flowing He. Using both normalization parameters, FeMoP, CoMoP, and NiMoP all show similar rates. However, RuMoP has the highest rate

compared to the other three materials, which is likely due to the noble metal behavior associated with inclusion of Ru to form the bimetallic solid solution.

3.3.3 Low temperature studies (125 – 250 °C) and cascade reactor configurations

A high selectivity to the DDO pathway can be achieved using FeMoP at 400°C and 750 psig H₂ pressure. However, HDO can also be achieved through the HYD pathway (Scheme 1b), which is more thermodynamically favored at lower reaction temperatures.⁶⁷ Therefore, the four materials were also tested at low temperature. Initial studies showed that FeMoP and CoMoP were not active below 300°C and 200°C respectively, while NiMoP and RuMoP showed catalytic activity at 125°C with cyclohexanol (>99% selectivity) as the major product. The deoxygenation ability of the materials at low temperature was tested by varying the residence time of the phenol while keeping other variables constant. The goal of the study was to increase the contact time between cyclohexanol with the more acidic surface to form more of the dehydration product (cyclohexene). However, as shown in Figure A.3, the results of the residence time study at 125°C on (a) NiMoP and (b) RuMoP showed that only cyclohexanol was formed even at higher contact times.

3.3.4 Cascade reaction in flow reactor

Lercher and co-workers have shown multistep HDO using various catalysts where the first step involves hydrogenation to cyclohexanone and cyclohexanol using Pd/C followed by dehydration using an acidic material such

as HZSM-5 and further hydrogenation using Pd/C all at reaction temperatures of 200°C.⁶⁸ Although RuMoP has the highest acid density relative to NiMoP, the acid strength in both materials were low and were not able to perform cyclohexanol dehydration under these reaction conditions. However, from our previous work, we showed that the FeMoP was able to perform dehydration reactions at ~180°C.¹¹ However, FeMoP was not catalytically active at this temperature to perform the C-O cleavage step. Therefore, we strategically engineered the bed packing to perform deoxygenation at low temperature using two different bimetallic phosphide catalysts (RuMoP for hydrogenation to cyclohexanol and FeMoP for dehydration of cyclohexanol). The experiment involved series bed packing such that the reactant comes into contact with RuMoP to form cyclohexanol and subsequently with FeMoP to dehydrate the cyclohexanol to cyclohexene (Figure 3.9). The H₂ rich environment would further aid in subsequent hydrogenation to cyclohexane.

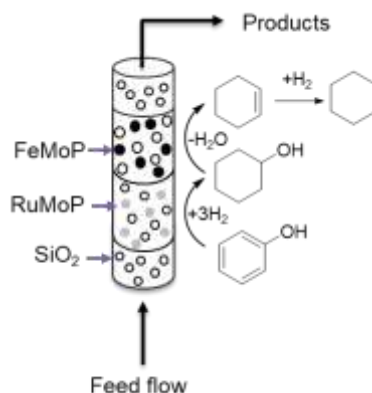


Figure 3.9. Cascade reactor design for phenol HDO with multiple bimetallic phosphide catalysts.

The bed was packed with equal masses of catalysts and diluted with SiO_2 to prevent thermal gradients. A temperature sweep was performed first to determine the temperature at which deoxygenation occurred. Figure 3.10a summarizes the experimental results of phenol HDO between 120°C and 260°C . Deoxygenation products (cyclohexane) were observed at 175°C , while benzene appears at 200°C . The observed benzene production originates from the DDO pathway through RuMoP since FeMoP is not active for HDO until 300°C . In all cases, cyclohexanol remains the dominating product. Another bed configuration was also tested where the two catalysts were mixed together and dispersed throughout the silica. As expected, the cyclohexane yield for the bed in series were higher compared to the mixed bed because the cyclohexanol produced from RuMoP has a higher contact time to the FeMoP catalysts in the series configuration. The experimental setup conveys the important result of performing cascade reactions with multiple transition metal phosphide catalysts.

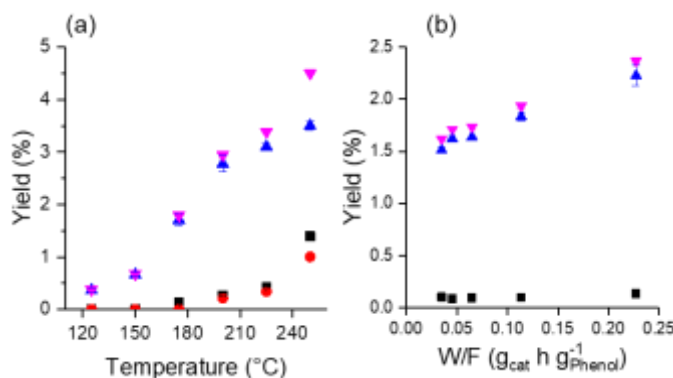


Figure 3.10. Yield of cyclohexanol (blue triangle), cyclohexane (black square), benzene (red circle), and overall conversion (magenta inverted triangle) of RuMoP and FeMoP in (a) temperature sweep and (b) W/F sweep at 175°C.

A last study was performed to see if the deoxygenation performance could be improved by increasing the contact time. The experimental result was obtained at 175°C (Figure 3.10b) using the same series bed configuration mentioned previously. Although the conversion increased, the formation of cyclohexane was stagnant due to limited amount of acid sites that can perform dehydration and its subsequent hydrogenation. Therefore, low temperature HDO is possible with a series of RuMoP and FeMoP catalysts in a flow system.

3.3.4 Cascade reactions in batch configuration

Although the cascade reaction in the flow system showed proof of concept for the cascade configuration, the yield was low due to the limitation in the reactor size. To showcase the cascade reaction capability with RuMoP and FeMoP at high conversions, the cascade reactions were also performed in the

250 mL Parr batch reactor to allow for longer reaction times and the ability to increase the catalyst loading more easily (Table 3.2).

RuMoP was studied at two different temperatures (175°C and 225°C) to identify any changes in the selectivity due to the reaction temperature. At 175°C and 99% conversion (Table 3.2, Entry 2), RuMoP was 93% selective towards the production of cyclohexanol, which decreased to 82% at 225°C (Table 3.2, Entry 4). It should also be noted that at 225°C, small quantities of benzene were observed (2%). Because RuMoP is highly selective to cyclohexanol, dehydration to cyclohexene using FeMoP was studied at 225°C (Table 3.2, Entries 5 and 6). As noted earlier, we have shown that the acidic nature of FeMoP catalyzes dehydration of cyclohexanol to cyclohexene in absence of H₂.¹¹ Therefore, using a 0.10 M feed solution of cyclohexanol in decane at 400 psig H₂ at 225°C, we observed a 62% selectivity to cyclohexene and a 38% selectivity to cyclohexane (Table 3.2, Entry 6). This result reiterates that FeMoP is able to dehydrate the cyclohexanol as well as subsequently hydrogenate cyclohexene to cyclohexane. Lastly, the overall cascade reaction of phenol to cyclohexane was performed by using a combination of RuMoP (70.0 mg) and FeMoP (70.0 mg), as shown in Table 3.2, Entries 7 and 8. At 99% phenol conversion (Table 3.2, Entry 8), the selectivity was 89%, 7%, and 4% to cyclohexane, cyclohexene, and benzene, respectively. It is possible that the benzene production was catalyzed by direct deoxygenation of phenol with RuMoP at 225°C based on the presence of benzene in Entries 3 and 4 in Table 3.2. Under these conditions, no cyclohexanol remained after 4 hours of reaction time, leading to complete

deoxygenation of phenol. The relative amounts of cyclohexane to cyclohexene in the final product provide evidence of further hydrogenation of cyclohexene to cyclohexane by RuMoP or FeMoP. Overall, the cascade reactions in the batch study demonstrated the deoxygenation ability of bimetallic phosphides at the temperature of 225°C.

TABLE 3.2.
CASCADE REACTION IN A 250 ML PARR BATCH REACTOR CHARGED
WITH A 400 PSIG H₂ PRESSURE AND A 30 ML OF 0.10 M REACTANT
CONCENTRATION FOR THE NOTED TIMES AND TEMPERATURES.

Entry	Catalyst	Catalyst amount (mg)	Reactant	T (°C)	t (h)	X (%)	S (%)				
											
1	RuMoP	70.0		175	10	78	0	0	5	95	-
2				175	15	99	0	0	7	93	-
3				225	2	20	2	3	8	85	2
4				225	10	99	2	2	14	82	-
5	FeMoP	70.0		225	10	82	-	74	26	-	-
6				225	13	99	-	62	38	-	-
7	RuMoP+ FeMoP	70.0 + 70.0		225	4	64	3	12	85	-	-
8				225	7	99	4	7	89	-	-

RuMoP was studied at two different temperatures (175°C and 225°C) to identify any changes in the selectivity due to the reaction temperature. At 175°C and 99% conversion (Table 3.2, Entry 2), RuMoP was 93% selective towards the production of cyclohexanol, which decreased to 82% at 225°C (Table 3.2, Entry

4). It should also be noted that at 225°C, small quantities of benzene were observed (2%). Because RuMoP is highly selective to cyclohexanol, dehydration to cyclohexene using FeMoP was studied at 225°C (Table 3.2, Entries 5 and 6). As noted earlier, we have shown that the acidic nature of FeMoP catalyzes dehydration of cyclohexanol to cyclohexene in absence of H₂.¹¹ Therefore, using a 0.10 M feed solution of cyclohexanol in decane at 400 psig H₂ at 225°C, we observed a 62% selectivity to cyclohexene and a 38% selectivity to cyclohexane (Table 3.2, Entry 6). This result reiterates that FeMoP is able to dehydrate the cyclohexanol as well as subsequently hydrogenate cyclohexene to cyclohexane. Lastly, the overall cascade reaction of phenol to cyclohexane was performed by using a combination of RuMoP (70.0 mg) and FeMoP (70.0 mg), as shown in Table 3.2, Entries 7 and 8. At 99% phenol conversion (Table 3.2, Entry 8), the selectivity was 89%, 7%, and 4% to cyclohexane, cyclohexene, and benzene, respectively. It is possible that the benzene production was catalyzed by direct deoxygenation of phenol with RuMoP at 225°C based on the presence of benzene in Entries 3 and 4 in Table 3.2. Under these conditions, no cyclohexanol remained after 4 hours of reaction time, leading to complete deoxygenation of phenol. The relative amounts of cyclohexane to cyclohexene in the final product provide evidence of further hydrogenation of cyclohexene to cyclohexane by RuMoP or FeMoP. Overall, the cascade reactions in the batch study demonstrated the deoxygenation ability of bimetallic phosphides at the temperature of 225°C.

3.4 Conclusion

Four unsupported molybdenum based bimetallic phosphides $MMoP$ ($M = Fe, Co, Ni, Ru$) were successfully synthesized and characterized. A linear relationship was observed between the binding energy shift from XPS and the electronegativity difference between P and the metals in the bimetallic phosphides $MMoP$ across the periodic table ($M = Fe, Co, Ni$). The same trend was also observed through the absorption energy shift in XANES. The Mo in $FeMoP$ is the most oxidized, and phenol HDO using this material yielded the highest DDO product (90%) followed by $RuMoP > CoMoP > NiMoP$ indicating that the relative oxidation of Mo plays an important role in directing the product selectivity. Low temperature (125°C) catalytic testing shows that the hydrogenation pathway is highly preferred (99% cyclohexanol selectivity) in $RuMoP$ and $NiMoP$, while $FeMoP$ and $CoMoP$ are inactive at these reaction conditions. Further studies show that HDO can be achieved at lower temperatures with cascade reactions in the flow and batch reactors with $RuMoP$ to yield cyclohexanol followed by $FeMoP$ for the subsequent dehydration and hydrogenation to produce cyclohexane.

3.5 References

1. Hicks, J. C., Advances in C-O Bond Transformations in Lignin-Derived Compounds for Biofuels Production. *J. Phys. Chem. Lett.* **2011**, 2 (18), 2280-2287.
2. Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A., Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chem. Soc. Rev.* **2012**, 41 (24), 8075-8098.

3. Robinson, A. M.; Hensley, J. E.; Medlin, J. W., Bifunctional catalysts for upgrading of biomass-derived oxygenates: a review. *ACS Catal.* **2016**, 6 (8), 5026-5043.
4. Neumann, G. T.; Hicks, J. C., Novel hierarchical cerium-incorporated MFI zeolite catalysts for the catalytic fast pyrolysis of lignocellulosic biomass. *ACS Catal.* **2012**, 2 (4), 642-646.
5. Kim, J.; Neumann, G. T.; McNamara, N. D.; Hicks, J. C., Exceptional control of carbon-supported transition metal nanoparticles using metal-organic frameworks. *J Mater Chem A* **2014**, 2 (34), 14014-14027.
6. Neumann, G. T.; Pimentel, B. R.; Rensel, D. J.; Hicks, J. C., Correlating lignin structure to aromatic products in the catalytic fast pyrolysis of lignin model compounds containing beta-O-4 linkages. *Catal. Sci. Technol.* **2014**, 4 (11), 3953-3963.
7. Anderson, E.; Crisci, A.; Murugappan, K.; Roman-Leshkov, Y., Bifunctional molybdenum polyoxometalates for the combined hydrodeoxygenation and alkylation of lignin-derived model phenolics. *ChemSusChem* **2017**, 10 (10), 2226-2234.
8. Zhong, J. W.; Chen, J. Z.; Chen, L. M., Selective hydrogenation of phenol and related derivatives. *Catal. Sci. Technol.* **2014**, 4 (10), 3555-3569.
9. Robinson, A.; Ferguson, G. A.; Gallagher, J. R.; Cheah, S.; Beckham, G. T.; Schaidle, J. A.; Hensley, J. E.; Medlin, J. W., Enhanced hydrodeoxygenation of m-cresol over bimetallic Pt-Mo catalysts through an oxophilic metal-induced tautomerization pathway. *ACS Catal.* **2016**, 6 (7), 4356-4368.
10. Mortensen, P. M.; Grunwaldt, J. D.; Jensen, P. A.; Knudsen, K. G.; Jensen, A. D., A review of catalytic upgrading of bio-oil to engine fuels. *Appl. Catal. A* **2011**, 407 (1-2), 1-19.
11. Rensel, D. J.; Kim, J.; Bonita, Y.; Hicks, J. C., Investigating the multifunctional nature of bimetallic FeMoP catalysts using dehydration and hydrogenolysis reactions. *Appl. Catal. A* **2016**, 524, 85-93.
12. Abu, I. I.; Smith, K. J., HDN and HDS of model compounds and light gas oil derived from Athabasca bitumen using supported metal phosphide catalysts. *Appl. Catal. A* **2007**, 328 (1), 58-67.
13. Li, K. L.; Wang, R. J.; Chen, J. X., Hydrodeoxygenation of Anisole over Silica-Supported Ni₂P, MoP, and NiMoP Catalysts. *Energ. Fuel* **2011**, 25 (3), 854-863.

14. Lee, Y. K.; Oyama, S. T., Bifunctional nature of a SiO₂-supported Ni₂P catalyst for hydrotreating: EXAFS and FTIR studies. *J. Catal.* **2006**, 239 (2), 376-389.
15. Stinner, C.; Prins, R.; Weber, T., Binary and ternary transition-metal phosphides as HDN catalysts. *J. Catal.* **2001**, 202 (1), 187-194.
16. Sun, F. X.; Wu, W. C.; Wu, Z. L.; Guo, J.; Wei, Z. B.; Yang, Y. X.; Jiang, Z. X.; Tian, F. P.; Li, C., Dibenzothiophene hydrodesulfurization activity and surface sites of silica-supported MoP, Ni₂P, and Ni-Mo-P catalysts. *J. Catal.* **2004**, 228 (2), 298-310.
17. Nagai, M.; Fukiage, T.; Kurata, S., Hydrodesulfurization of dibenzothiophene over alumina-supported nickel molybdenum phosphide catalysts. *Catal. Today.* **2005**, 106 (1-4), 201-205.
18. Rui, W.; Smith, K. J., Hydrodesulfurization of 4,6-dimethyldibenzothiophene over high surface area metal phosphides. *Appl. Catal. A* **2009**, 361 (1-2), 18-25.
19. Li, X.; Bai, J.; Wang, A. J.; Prins, R.; Wang, Y., Hydrodesulfurization of dibenzothiophene and its hydrogenated intermediates over bulk Ni₂P. *Top. Catal.* **2011**, 54 (5-7), 290-298.
20. Oyama, S. T., Novel catalysts for advanced hydroprocessing: transition metal phosphides. *J. Catal.* **2003**, 216 (1-2), 343-352.
21. Rensel, D. J.; Rouvimov, S.; Gin, M. E.; Hicks, J. C., Highly selective bimetallic FeMoP catalyst for C-O bond cleavage of aryl ethers. *J. Catal.* **2013**, 305, 256-263.
22. Chang, S. A.; Flaherty, D. W., Mechanistic Study of Formic Acid Decomposition over Ru(0001) and P-X-Ru(0001): Effects of Phosphorus on C-H and C-O Bond Rupture. *J. Phys. Chem. C* **2016**, 120 (44), 25425-25435.
23. Bowker, R. H.; Smith, M. C.; Pease, M. L.; Slenkamp, K. M.; Kovarik, L.; Bussell, M. E., Synthesis and hydrodeoxygenation properties of ruthenium phosphide catalysts. *ACS Catal.* **2011**, 1 (8), 917-922.
24. Tan, Q. H.; Wang, G. H.; Nie, L.; Dinse, A.; Buda, C.; Shabaker, J.; Resasco, D. E., Different product distributions and mechanistic aspects of the hydrodeoxygenation of m-cresol over platinum and ruthenium catalysts. *ACS Catal.* **2015**, 5 (11), 6271-6283.

25. Tan, Q. H.; Wang, G. H.; Long, A.; Dinse, A.; Buda, C.; Shabaker, J.; Resasco, D. E., Mechanistic analysis of the role of metal oxophilicity in the hydrodeoxygenation of anisole. *J. Catal.* **2017**, *347*, 102-115.
26. Gutierrez, A.; Kaila, R. K.; Honkela, M. L.; Slioor, R.; Krause, A. O. I., Hydrodeoxygenation of guaiacol on noble metal catalysts. *Catal. Today.* **2009**, *147* (3-4), 239-246.
27. Wang, C. L.; Wu, Z. Z.; Tang, C. Y.; Li, L. H.; Wang, D. Z., The effect of nickel content on the hydrodeoxygenation of 4-methylphenol over unsupported NiMoW sulfide catalysts. *Catal. Commun.* **2013**, *32*, 76-80.
28. Bui, V. N.; Laurenti, D.; Afanasiev, P.; Geantet, C., Hydrodeoxygenation of guaiacol with CoMo catalysts. Part I: Promoting effect of cobalt on HDO selectivity and activity. *Appl. Catal. B* **2011**, *101* (3-4), 239-245.
29. Centeno, A.; Laurent, E.; Delmon, B., Influence of the support of CoMo sulfide catalysts and of the addition of potassium and platinum on the catalytic performances for the hydrodeoxygenation of carbonyl, carboxyl, and guaiacol-type molecules. *J. Catal.* **1995**, *154* (2), 288-298.
30. Jongerius, A. L.; Jastrzebski, R.; Bruijnincx, P. C. A.; Weckhuysen, B. M., CoMo sulfide-catalyzed hydrodeoxygenation of lignin model compounds: An extended reaction network for the conversion of monomeric and dimeric substrates. *J. Catal.* **2012**, *285* (1), 315-323.
31. Shetty, M.; Murugappan, K.; Prasomsri, T.; Green, W. H.; Roman-Leshkov, Y., Reactivity and stability investigation of supported molybdenum oxide catalysts for the hydrodeoxygenation (HDO) of m-cresol. *J. Catal.* **2015**, *331*, 86-97.
32. Boullosa-Eiras, S.; Lodeng, R.; Bergem, H.; Stocker, M.; Hannevold, L.; Blekkana, E. A., Catalytic hydrodeoxygenation (HDO) of phenol over supported molybdenum carbide, nitride, phosphide and oxide catalysts. *Catal. Today.* **2014**, *223*, 44-53.
33. Kallury, R. K. M. R.; Restivo, W. M.; Tidwell, T. T.; Boocock, D. G. B.; Crimi, A.; Douglas, J., Hydrodeoxygenation of hydroxy, methoxy, and methyl phenols with molybdenum oxide nickel-oxide alumina catalyst. *J. Catal.* **1985**, *96* (2), 535-543.
34. Lee, W. S.; Wang, Z. S.; Wu, R. J.; Bhan, A., Selective vapor-phase hydrodeoxygenation of anisole to benzene on molybdenum carbide catalysts. *J. Catal.* **2014**, *319*, 44-53.
35. Ren, H.; Yu, W. T.; Saliccioli, M.; Chen, Y.; Huang, Y. L.; Xiong, K.; Vlachos, D. G.; Chen, J. G. G., Selective hydrodeoxygenation of biomass-

derived oxygenates to unsaturated hydrocarbons using molybdenum carbide catalysts. *ChemSusChem* **2013**, 6 (5), 798-801.

36. Xiong, K.; Lee, W. S.; Bhan, A.; Chen, J. G. G., Molybdenum Carbide as a Highly Selective Deoxygenation Catalyst for Converting Furfural to 2-Methylfuran. *ChemSusChem* **2014**, 7 (8), 2146-2149.
37. Rensel, D. J.; Kim, J.; Jain, V.; Bonita, Y.; Rai, N.; Hicks, J. C., Composition-directed $\text{Fe}_x\text{Mo}_{2-x}\text{P}$ bimetallic catalysts for hydrodeoxygenation reactions. *Catal. Sci. Technol.* **2017**, 7, 1857-1867.
38. Chen, J. X.; Yang, Y.; Shi, H.; Li, M. F.; Chu, Y.; Pan, Z. Y.; Yu, X. B., Regulating product distribution in deoxygenation of methyl laurate on silica-supported Ni-Mo phosphides: Effect of Ni/Mo ratio. *Fuel* **2014**, 129, 1-10.
39. Cho, A.; Shin, J.; Takagaki, A.; Kikuchi, R.; Oyama, S. T., Ligand and ensemble effects in bimetallic NiFe phosphide catalysts for the hydrodeoxygenation of 2-methyltetrahydrofuran. *Top. Catal.* **2012**, 55 (14-15), 969-980.
40. Khattak, G. D.; Salim, M. A.; AlHarthi, A. S.; Thompson, D. J.; Wenger, L. E., Structure of molybdenum-phosphate glasses by X-ray photoelectron spectroscopy (XPS). *J. Non-Cryst. Solids.* **1997**, 212 (2-3), 180-191.
41. Phillips, D. C.; Sawhill, S. J.; Self, R.; Bussell, M. E., Synthesis, characterization, and hydrodesulfurization properties of silica-supported molybdenum phosphide catalysts. *J. Catal.* **2002**, 207 (2), 266-273.
42. Zuzaniuk, V.; Prins, R., Synthesis and characterization of silica-supported transition-metal phosphides as HDN catalysts. *J. Catal.* **2003**, 219 (1), 85-96.
43. Zhou, T.-n.; Yin, H.-l.; Han, S.-n.; Chai, Y.-m.; Liu, Y.-q.; Liu, C.-g., Influences of different phosphorus contents on NiMoP/Al₂O₃ hydrotreating catalysts. *J. Fuel Chem. Technol.* **2009**, 37 (3), 330-334.
44. Shabtai, J.; Nag, N. K.; Massoth, F. E., Catalytic functionalities of supported sulfides. 4. C-O hydrogenolysis selectivity as a function of promoter type. *J. Catal.* **1987**, 104 (2), 413-423.
45. Oyama, S. T.; Gott, T.; Zhao, H. Y.; Lee, Y. K., Transition metal phosphide hydroprocessing catalysts: A review. *Catal. Today.* **2009**, 143 (1-2), 94-107.
46. Aronsson, B.; Lundstrom, T.; Rundqvist, S., *Borides, silicides, and phosphides*. Methuen, London: Wiley: New York, 1965.

47. Oyama, S. T.; Lee, Y. K., The active site of nickel phosphide catalysts for the hydrodesulfurization of 4,6-DMDBT. *J. Catal.* **2008**, 258 (2), 393-400.
48. Gaudette, A. F.; Burns, A. W.; Hayes, J. R.; Smith, M. C.; Bowker, R. H.; Seda, T.; Bussell, M. E., Mossbauer spectroscopy investigation and hydrodesulfurization properties of iron-nickel phosphide catalysts. *J. Catal.* **2010**, 272 (1), 18-27.
49. Wang, R.; Smith, K. J., Preparation of Unsupported NiMoP Catalysts for 4,6-Dimethyldibenzothiophene Hydrodesulfurization. *Catal. Lett.* **2014**, 144 (9), 1594-1601.
50. Layman, K. A.; Bussell, M. E., Infrared spectroscopic investigation of CO adsorption on silica-supported nickel phosphide catalysts. *J. Phys. Chem. B* **2004**, 108 (30), 10930-10941.
51. Blanchard, P. E. R.; Grosvenor, A. P.; Cavell, R. G.; Mar, A., Effects of metal substitution in transition-metal phosphides (Ni_{1-x}M'(x))(2)P (M' = Cr, Fe, Co) studied by X-ray photoelectron and absorption spectroscopy. *J. Mater. Chem.* **2009**, 19 (33), 6015-6022.
52. Grosvenor, A. P.; Wik, S. D.; Cavell, R. G.; Mar, A., Examination of the bonding in binary transition-metal monophosphides MP (M = Cr, Mn, Fe, Co) by x-ray photoelectron spectroscopy. *Inorg. Chem.* **2005**, 44 (24), 8988-8998.
53. Grosvenor, A. P.; Cavell, R. G.; Mar, A., Next-nearest neighbour contributions to P 2p(3/2) X-ray photoelectron binding energy shifts of mixed transition-metal phosphides M_{1-x}M'P_x with the MnP-type structure. *J. Solid State Chem.* **2007**, 180 (10), 2702-2712.
54. Blanchard, P. E. R.; Grosvenor, A. P.; Cavell, R. G.; Mar, A., X-ray photoelectron and absorption spectroscopy of metal-rich phosphides M₂P and M₃P (M = Cr-Ni). *Chem. Mater.* **2008**, 20 (22), 7081-7088.
55. Pelavin, M.; Hendrickson, D. N.; Hollander, J. M.; Jolly, W. L., Phosphorus 2p electron binding energies: correlation with extended Huckel charges. *J. Phys. Chem.* **1970**, 74 (5).
56. Grosvenor, A. P.; Cavell, R. G.; Mar, A., Bonding and electronic structure of phosphides, arsenides, and antimonides by x-ray photoelectron and absorption spectroscopies. *Struct Bond* **2009**, 133, 41-92.
57. Whiffen, V. M. L.; Smith, K. J., Hydrodeoxygenation of 4-Methylphenol over Unsupported MoP, MoS₂, and MoO_x Catalysts. *Energ. Fuel* **2010**, 24, 4728-4737.

58. Doniach, S.; Sunjic, M., Many-electron singularity in x-ray photoemission and x-ray line spectra from metals. *J. Phys. C*. **1970**, 3 (2), 285-&.
59. Allred, A. L.; Rochow, E. G., A scale of electronegativity based on electrostatic force. *J. Inorg. Nucl. Chem.* **1958**, 5 (4), 264-268.
60. Ressler, T.; Wienold, J.; Jentoft, R. E.; Neisius, T., Bulk structural investigation of the reduction of MoO₃ with propene and the oxidation of MoO₂ with oxygen. *J. Catal.* **2002**, 210 (1), 67-83.
61. de Souza, P. M.; Nie, L.; Borges, L. E. P.; Noronha, F. B.; Resasco, D. E., Role of oxophilic supports in the selective hydrodeoxygenation of m-cresol on Pd catalysts. *Catal. Lett.* **2014**, 144 (12), 2005-2011.
62. Teles, C. A.; Rabelo-Neto, R. C.; de Lima, J. R.; Mattos, L. V.; Resasco, D. E.; Noronha, F. B., The effect of metal type on hydrodeoxygenation of phenol over silica supported catalysts. *Catal. Lett.* **2016**, 146 (10), 1848-1857.
63. Barkdoll, A. E.; England, D. C.; Gray, H. W.; Kirk, W.; Whitman, G. M., Alicyclic diamines - preparation of bis-(4-aminocyclohexyl)-methane. *J. Am. Chem. Soc.* **1953**, 75 (5), 1156-1159.
64. Freifelder, M.; Stone, G. R., Reductions with ruthenium catalysts .1. Preparation of some cyclohexylalkylamines. *J. Am. Chem. Soc.* **1958**, 80 (19), 5270-5272.
65. Su, F. B.; Lee, F. Y.; Lv, L.; Liu, J. J.; Tian, X. N.; Zhao, X. S., Sandwiched ruthenium/carbon nanostructures for highly active heterogeneous hydrogenation. *Adv. Funct. Mater.* **2007**, 17 (12), 1926-1931.
66. Corro, G.; Gomez, R., Carbon-monoxide adsorption and hydrogen-oxygen titration on Ru-Al₂O₃. *React. Kinet. Catal. L.* **1979**, 12 (2), 145-150.
67. Shin, E. J.; Keane, M. A., Gas-phase hydrogenation/hydrogenolysis of phenol over supported nickel catalysts. *Ind. Eng. Chem. Res.* **2000**, 39 (4), 883-892.
68. He, J.; Zhao, C.; Lercher, J. A., Impact of solvent for individual steps of phenol hydrodeoxygenation with Pd/C and HZSM-5 as catalysts. *J. Catal.* **2014**, 309, 362-375.

CHAPTER 4

REVEALING THE HYDROGENATION PERFORMANCE OF RUMO PHOSPHIDE FOR CHEMOSELECTIVE REDUCTION OF FUNCTIONALIZED AROMATIC HYDROCARBONS[†]

4.1 Introduction

As described in the introduction chapter, selective hydrogenation reactions are highly important chemical transformations for the production of chemicals and the upgrading of lignocellulosic biomass.¹ This chapter aims to understand how newly discovered catalysts interact with molecules containing multiple functionalities is warranted.

Many catalysts such as supported Au, Pd, Pt, and Ru have been studied for hydrogenation reactions of compounds with multiple functionalities such as nitro aromatics, aromatic rings, and carbonyls.¹¹⁻¹⁹ Another material that is active for hydrogenation reactions, yet its potential remains significantly underexplored, is metal phosphides. For example, Ni₂P has been used as a catalyst for the hydrogenation of butadiene to make butene isomers, hydrodesulfurization,

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carbonyl reduction to form alcohols from aldehydes, and nitrobenzene reduction to aniline.^{3, 20-23} Nevertheless, the selectivity towards C=O reduction or aniline-based compounds are still low due to the competing hydrogenation reactions occurring within the substrate.²²⁻²³ Efforts to improve the selectivity include altering the electronic properties of the metal phosphide by chemical anchoring to a support.³ However, the electronic properties can also be altered synthetically through the addition of another metal to form a bimetallic phosphide.²⁴⁻²⁵

In Chapter 3, we reported bimetallic RuMoP exhibited high ring hydrogenation selectivity (99%) towards cyclohexanol at low reaction temperature (125°C).²⁵ Using experiments and theory, the partially positive nature of the metals in RuMoP was suggested as the responsible site for aromatic ring adsorption and the resulting ring hydrogenation.²⁶ However, product selectivity is not only dependent on the nature of the active sites but also the electronic distribution of the reactant.¹² In phenol, the hydroxyl group acts as an electron donator to the aromatic ring, causing the ring to become more electron rich, which could contribute to the preferential adsorption of the ring on the surface. Therefore, variation of the functional group can alter the interaction between the reactant and the surface.

The scope of this work includes the examination of RuMoP as a catalyst for chemoselective hydrogenation of aromatic hydrocarbons with either electron withdrawing or electron donating groups. The catalytic performance of RuMoP is also studied for aromatic hydrocarbons containing multiple substituents.

Additionally, the surface interaction between the substrates and the catalyst

surface is probed using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to gain insight to the coordination environment of competing functionalities.

4.2 Experimental

4.2.1 Materials

Citric acid monohydrate (Amresco, 99%), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 99%), $(\text{NH}_4)_2\text{HPO}_4$ (Amresco, 99%), $\text{RuCl}_3\cdot x\text{H}_2\text{O}$ (Oakwood Chemicals, 99%), KBr (Alfa Aesar, 99%), isopropanol (J.T. Baker, 99.5%), nitrobenzene (Alfa Aesar, 99%), aniline (Sigma Aldrich, 99%), benzaldehyde (Sigma Aldrich, 99.5%), toluene (Macron, 99.5%), benzyl alcohol (Alfa Aesar, 99%), phenol (Sigma Aldrich, 99%), cyclohexanol (Alfa Aesar, 99%), anisole (Alfa Aesar, 99%), methylcyclohexane (TCI Chemicals, 99%), methyl benzoate (Alfa Aesar, 99%), p-nitroanisole (Sigma Aldrich, 97%), p-nitrophenol (TCI, 99%), n-decane (Alfa Aesar, 99%), H_2 (Airgas, 99.999%), N_2 (Airgas, 99.998%), 30%CO in He (Airgas, 99.99%), 1% O_2 in He (Airgas, 99.99%)

4.2.2 Catalyst synthesis and characterization

The RuMoP catalyst used in this study was synthesized according to the synthetic methods developed in our group as described previously.²⁵⁻²⁶ In a typical synthesis, 7 mmol of citric acid was added to 50 mL of deionized water. After the citric acid was dissolved, 1.2 mmol of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was dissolved in the same solution followed by the addition of 5 mmol $\text{RuCl}_3\cdot x\text{H}_2\text{O}$

and 5 mmol $(\text{NH}_4)_2\text{HPO}_4$. After stirring for one hour, the solution was evaporated to approximately 25 mL using a rotary evaporator. The resulting slurry was subsequently dried at 200°C for 2 h at 1°C/min ramp rate. The cake formed after drying was then ground and calcined at 550°C for 6 h with a 1°C/min ramp rate. After the calcination step, the powder was reduced under 160 mL/min H_2 flow at 650°C for 2 h with 5°C/min ramp rate. The resulting powder was pyrophoric and thus a passivation step using 160 mL/min of 1% O_2 in He for 1 h was performed before transferring the sample into a N_2 dry box for storage.

The crystal structure was confirmed using a Bruker D8 Advance Davinci powder x-ray diffractometer (XRD). The diffraction pattern was collected between 20° - 60° 2θ with 0.02° step size, scanning speed of 2 s per step, and 15°/min rotation using ~50 mg sample with no further pretreatment. The surface area of the material was measured using a Quantachrome NOVA 2000e N_2 physisorption instrument. Prior to the analysis, ~0.25 g the sample as degassed overnight under vacuum at 125°C. The composition of the metals was quantified with an Optima 8000 inductively coupled plasma – optical emission spectroscopy (ICP-OES) instrument with external calibration. The active site of the catalyst was titrated using a Micromeritics Chemisorb 2750 with CO pulse chemisorption experiment. The sample (~0.2 g) was pretreated under 30 mL/min of H_2 at 400°C for 2 h followed by 30 mL/min of He at 400°C for 1.5 h. The last pretreatment step was at 100°C at 30 mL/min H_2 flow to prevent polycarbonyl formation.²⁷ The CO pulse injections were performed at 35°C with 0.1 mL injections.

The nature of the surface sites in RuMoP was probed using a Bruker Vertex 70 equipped with Harrick Praying Mantis high pressure cell for diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements. The detector used in this study was a mercury-cadmium-telluride (MCT) detector cooled with liquid N₂. The sample cup was packed with 80 mg of KBr and 20 mg of the RuMoP samples on top of it. The KBr was used to lift the samples, but they are not mixed. The sample was lightly pressed to form a flat surface. Prior to analysis, pure RuMoP was reduced *in situ* with 30 mL/min H₂ flow at 400°C for 2 h. After the pretreatment, the material was cooled down under a 30 mL/min flow of N₂ and background scans were collected simultaneously at 400°C, 300°C, 200°C, 100°C and 50°C. Pyridine was used as a probe molecule for the surface acid sites and was exposed to the catalyst by flowing N₂ through a pyridine bubbler maintained at room temperature for 1 hr. After saturation with pyridine, the cell was flushed with N₂ for 10 mins and spectra were collected at different temperatures using 4 cm⁻¹ resolution with the appropriate background scans collected during cooling. The procedure was repeated using other adsorbates such as nitrobenzene, anisole, isopropanol, and p-nitroanisole using fresh catalysts for each experiment. The saturation temperature for these adsorbates was 100°C.

4.2.3 Catalyst testing

The catalyst was tested in both flow and batch reactor configurations. The flow reaction was conducted in an up-flow quarter inch 316 stainless steel tube

equipped with a 10 μm stainless steel mesh screen at the top to prevent the catalyst from moving downstream from the reaction zone. In a typical experiment, 50.0 mg of 60-100 mesh SiO_2 gel was loaded into the reactor followed with 120.0 mg SiO_2 gel mixed with 30.0 mg of RuMoP and 25.0 mg of SiO_2 . The bottom of the catalyst bed was held using 10.0 mg of quartz wool. Two thermocouples were installed on top and bottom of the reactor bed to ensure temperature control throughout the catalyst bed. The catalyst was pre-treated at 400°C for 1 h under 100 mL/min of H_2 flow and cooled down to reaction temperature (125°C) rapidly. After the desired temperature was reached, the reactor was pressurized to 4.1 MPa H_2 , and the liquid feed (0.02 M reactant in isopropanol) was flowed at 1.2 mL/min – 0.2 mL/min. After the reaction reached steady state, three consecutive liquid samples were taken and analyzed using an Agilent Gas Chromatograph 7890A – Mass Spectrometer 5975C (GCMS) with an external calibration. The reaction result is reported as a function of W/F defined in Equation 1 where g_{cat} is the mass of catalyst (g), N_{CO} is the moles of CO-accessible sites in RuMoP per gram (mol/g) and F_{reactant} is the molar flowrate of the reactant (mol/s).

$$\frac{W}{F} = \frac{m_{\text{cat}} N_{\text{CO}}}{F_{\text{reactant}}} \quad (\text{Equation 4.1})$$

A batch reactor was used for reactions that were slower, required more catalyst, or required a longer reaction time. In a typical experiment, 40.0 mg of RuMoP was loaded into a 300 mL high pressure Parr batch reactor followed immediately by the addition of 40 mL of 0.02 M reactant in isopropanol. The

reactor was sealed and purged three times with 4.1 MPa N₂ followed by three purges with 4.1 MPa H₂. The reactor was heated to 125°C with a Parr 4848 temperature controller. After the reactor reached the reaction temperature, 4.1 MPa of H₂ was fed into the reactor and this point was marked as $t = 0$. Afterwards, 100 μ L samples were taken throughout the reaction using a custom internal liquid sampler and condenser.

4.3 Result and discussion

4.3.1 Bulk and surface characterization of RuMoP

RuMoP was synthesized via temperature programmed reduction, as described in the previous section, to form the orthorhombic crystal structure confirmed by powder XRD (Figure 1). The diffraction pattern matches the reference data with (112), (211), (301), (020), (111), and (102) planes observed. The XRD pattern of orthorhombic RuMoP is distinct from patterns associated with monometallic MoP (PDF 04-002-4743), Mo₃P (PDF 03-065-1609), and RuP (PDF 04-004-3077). Using a Si(111) standard during analysis, orthorhombic Ru₂P (PDF 04-004-4140) was not observed because the peak position of RuMoP(112) was shifted to 37.9° 2 θ due to the incorporation of Mo into the lattice. Without bimetallic formation, Ru₂P(211) is located at 38.2° 2 θ . The shift to a smaller 2 θ indicates larger unit cell due to the incorporation of Mo. Moreover, the lack of Ru₂P peak at 40.6° 2 θ is showing that Ru₂P is not present in the sample. Therefore, the diffraction pattern in **Figure 4.1**. Diffraction pattern of RuMoP sample (red) in comparison to its reference pattern PDF 04-015-7732

(black) Figure 4.1 is confirmed as RuMoP. Additionally, ICP-OES was used to determine the bulk composition of the unsupported RuMoP powder, which provided a composition for Ru:Mo:P of 1.02: 0.99: 1.00. The number of CO sites determined with CO pulse chemisorption was determined as 20 $\mu\text{mol/g}$, and the Brunauer-Emmett-Teller (BET) surface area of the material was 12 m^2/g , which is in agreement with literature reports on unsupported phosphides.²⁴⁻²⁵

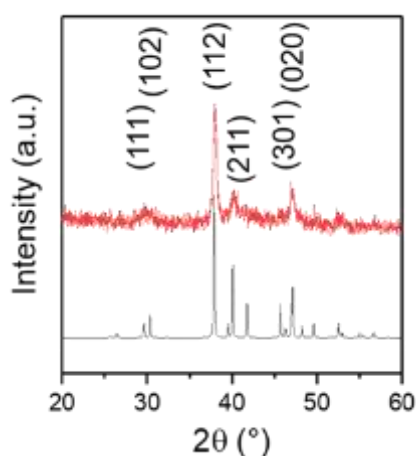


Figure 4.1. Diffraction pattern of RuMoP sample (red) in comparison to its reference pattern PDF 04-015-7732 (black).

The nature of the acid sites (Brønsted vs. Lewis acidity) in RuMoP was probed using DRIFTS of adsorbed pyridine serving as the probe molecule. Lewis acids present on the phosphide surface coordinatively bind to the N lone pair of pyridine, while Brønsted acid sites protonate the pyridine to form features characteristic of the pyridinium ion. The features associated with pyridine adsorption on Lewis acid sites (i.e., partially oxidized metal sites) were expected in the 1600-1633 cm^{-1} , 1488-1503 cm^{-1} , and 1447-1460 cm^{-1} regions.²⁸⁻³¹ The

Brønsted acidity resulting from surface P_xO_y-H species were expected in the $\sim 1640\text{ cm}^{-1}$, 1540 cm^{-1} , and $1485\text{--}1500\text{ cm}^{-1}$ regions.²⁸⁻³¹ The pretreatment and spectra collection procedure are described in section 4.2.2. The spectrum collected for the pyridine saturated RuMoP surface at 50°C is shown in Figure 4.2a. From this spectrum, physisorbed pyridine features are observed at 1440 cm^{-1} , 1572 cm^{-1} , and 1580 cm^{-1} , which correspond to $\nu[\text{CC}(\text{N})]$ type 19b, 8b, and 8a vibration modes in pyridine, respectively.^{29, 32} After saturation, the physisorbed pyridine was removed by flushing with N_2 for 10 mins (Figure 4.2b). As shown in Figure 4.2b, the features associated with physisorbed pyridine decrease in relative intensity compared to chemisorbed pyridine. After flushing for 30 mins, the relative intensity of the physisorbed peaks decrease further (Figure 4.2c), revealing mainly chemisorbed species. The decrease in relative intensity is even more apparent as the temperature is increased to 100°C and 200°C (Figure 4.2d, 4.2e). The interaction between pyridine and surface Lewis acid sites is observed from the $\nu[\text{CC}(\text{N})]$ type 19b and 8a vibration at 1448 cm^{-1} and 1610 cm^{-1} , respectively.³²⁻³⁴ The peak at 1488 cm^{-1} is assigned to both Lewis and Brønsted acid interactions, but the absence of the $\nu[\text{CC}(\text{N})]$ type 19b Brønsted acid feature at 1545 cm^{-1} indicates the primary adsorption mode between pyridine and RuMoP occurs from Lewis acid-type interactions.³⁴

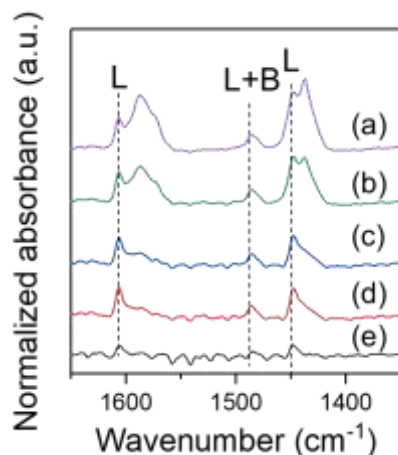


Figure 4.2. DRIFT spectra of pyridine adsorption at (a) saturation point, (b) after purging with N₂ at 50°C for 10 mins, (c) 50°C for 30 mins, (d) 100°C for 30 mins, and (e) 200°C for 30 mins. The dotted lines indicate pyridine adsorption on Lewis acid (L) and Brønsted acid (B).

In a separate study, pyridine hydrogenation reaction was tested in the batch reactor at 4.2 MPa with procedure described in the experimental section. The reaction was tested at 125°C – 200°C and samples were collected at 24 h reaction time. However, at these reaction conditions, no reaction products (i.e. piperidine) was observed. Catalyst deactivation through poisoning due to the basic nature of pyridine was observed. Catalyst deactivation through poisoning due to the basic nature of pyridine has been reported in the literature.³⁵ Similarly, acid site poisoning might occur in RuMoP. This is supported further with the pyridine DRIFTS study (Figure 4.2e), where at 200°C, peaks from pyridine – Lewis acid interaction can still be observed.

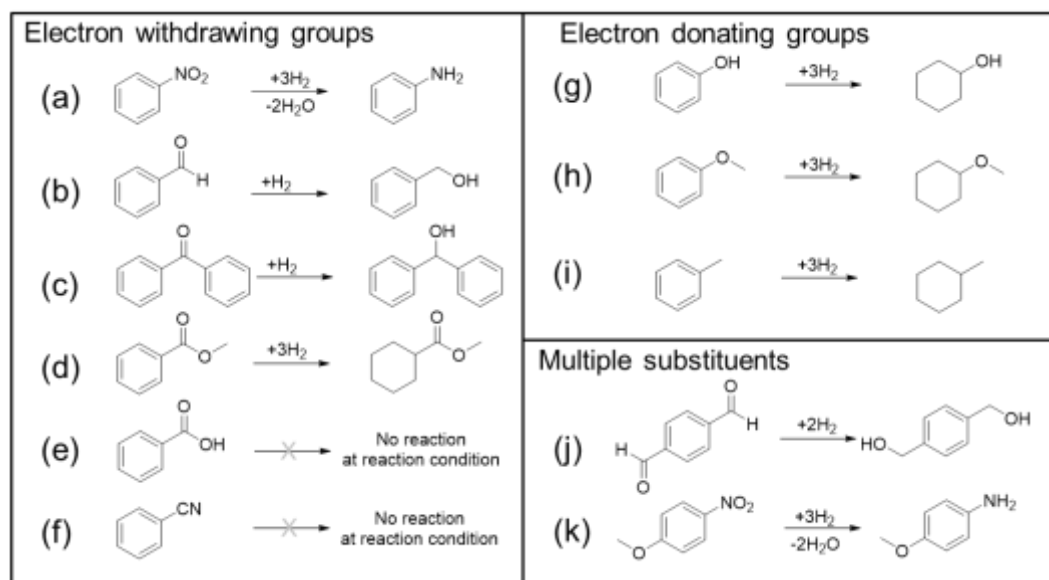
4.3.2 Aromatics possessing electron withdrawing substituents

To study the hydrogenation performance of RuMoP towards the electron withdrawing group on the aromatic ring, several functionalities such as nitro, aldehyde, ketone, ester, acid, and nitrile were examined. The molecules of

interest in this study are summarized in Scheme 1. For nitrobenzene (Scheme 1a), due to the N lone pair sharing with the two O attached, the N lone pair cannot be donated back into the ring, making NO₂ a strong withdrawing group.² Figure 4.3a shows the conversion (black) and selectivity (red) to aniline for nitrobenzene hydrogenation with varying W/F. As expected, the reaction proceeds with high selectivity towards aniline (>99%) with no ring hydrogenation product being observed even at complete conversion (Figure 4.3a). The high selectivity of nitrobenzene to aniline was also observed with nickel phosphide using NaBH₄ as the H-source.²³ Here we show the high selectivity towards aniline can also be achieved with gaseous molecular hydrogen, which is a cleaner H-source. Moreover, it has been suggested that nitrobenzene adsorption on the phosphide surface occurs through the -NO₂ group, which is discussed in more detail in Section 3.4.²³

The reduction of an aldehyde functionality to the corresponding primary alcohol was observed through benzaldehyde hydrogenation with RuMoP (Scheme 1b). The reaction result is shown in Figure 4.3b with conversion, selectivity to benzyl alcohol, and selectivity to toluene represented in black, red, and blue, respectively. According to the reaction result, RuMoP shows high selectivity towards benzyl alcohol (~99%) up until 30% conversion. Small amounts of toluene were observed past this conversion, which lowered the selectivity to ~97% at 48% conversion. Interestingly, it is reported that monometallic ruthenium phosphide Ru_xP participates in C-C bond cleavage of benzaldehyde to form benzene.³⁶ Similar C-C bond cleavage was also reported

in furan hydrodeoxygenation to form C3 and C4 products.³⁷ In this work, under the reaction conditions studied with RuMoP, no C-C bond cleavage was observed, which potentially suggests that the incorporation of Mo facilitates charge transfer and alters the electronic properties of the surface resulting in a weaker interaction between the substrates and the catalyst surface. Additionally, density functional theory (DFT) studies have calculated Mo as slightly positive in RuMoP, which suggests its role as the Lewis acid source needed for the required surface interaction.²⁶ The Lewis acidity character of RuMoP is corroborated from the DRIFTS study using pyridine, where Lewis acid binding sites were apparent in the spectra.



Scheme 4.1. Reaction summary for the hydrogenation of substituted aromatics using RuMoP with the corresponding major products at 125°C and 4.1 MPa.

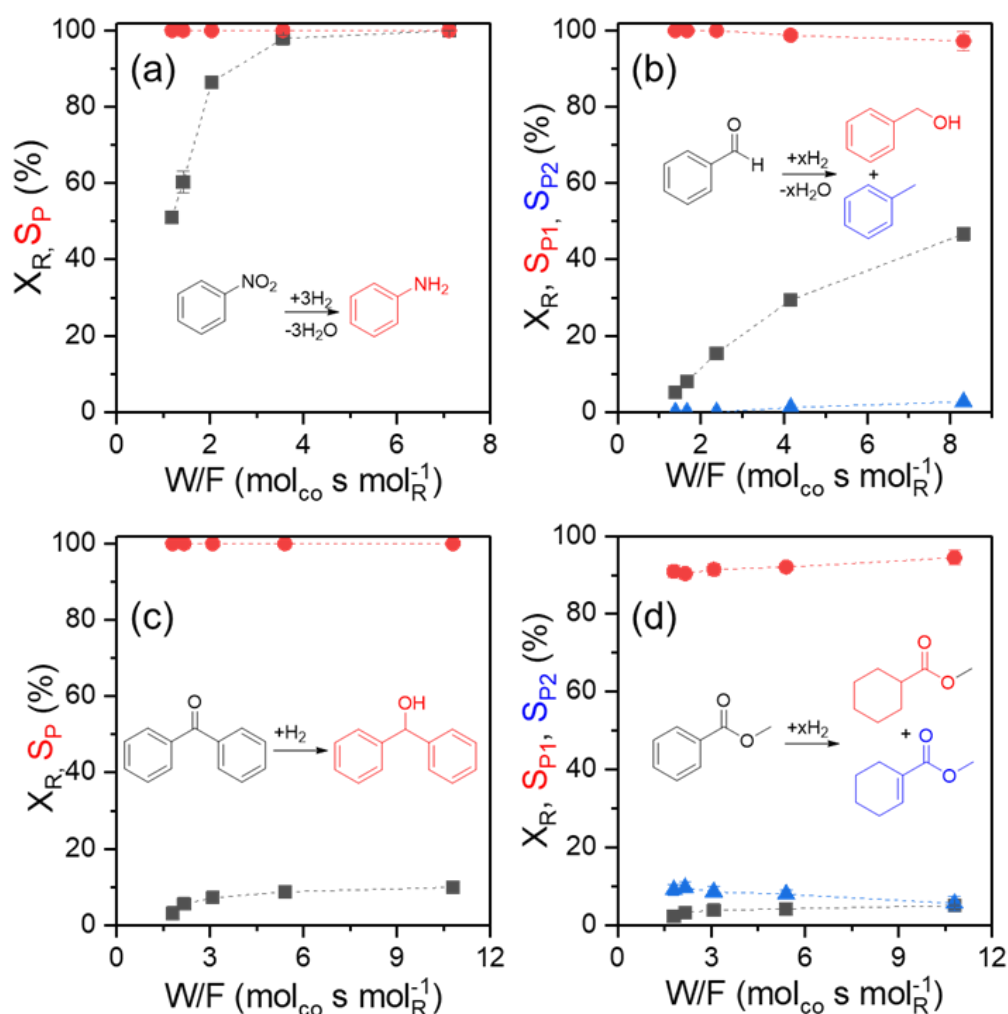


Figure 4.3. Conversion (black) and product selectivity (red, blue) of (a) nitrobenzene, (b) benzaldehyde, (c) benzophenone, and (d) methyl benzoate as a function of W/F .

Ketone hydrogenation to the corresponding alcohol could also occur on RuMoP since the catalyst could reduce the carbonyl in benzaldehyde. Therefore, benzophenone was used as a substrate in the reaction (Scheme 1c). Indeed, the hydrogenation of benzophenone yields diphenylmethanol with 99% selectivity, reducing only the carbonyl group (Figure 4.3c). The conversion is, however, low compared to benzaldehyde hydrogenation, which is likely due to steric effects

from the two benzene rings. Other solid catalysts have also been studied for selective reduction of carbonyl compounds includes oxides, zeolites, and supported metals.¹² Specifically, metals such as supported Pt, Au, Rh, Ni, Ag, Ir, and Os have also been studied for selective carbonyl reduction with Os/SiO₂ providing > 99% selectivity at 5 % conversion.^{12, 38} For Pt-based catalysts, selectivity to C=O reduction can be tuned by varying the support, particle size, or addition of other metals.^{12, 39-40}

Although RuMoP catalyst is able to reduce the electron withdrawing group functionality in aromatic compounds containing nitro groups, aldehydes, and ketones, RuMoP cannot reduce methyl benzoate (aromatic ester; Scheme 1d) under the conditions tested in this study (125°C and 4.1 MPa). Figure 4.3d depicts the conversion of methyl benzoate represented in black, the selectivity of methyl cyclohexanoate in red, and the selectivity of methyl 1-cyclohexenecarboxylate in blue. The hydrogenation of methyl benzoate results in the reduction of the phenyl ring to form methyl cyclohexanoate and methyl 1-cyclohexenecarboxylate, with the former being the more dominant product. Interestingly, RuMoP is not active for carboxylic acid (i.e. 3,5-dicarboxylic acid) hydrogenation at the same reaction condition. In the reduction of carboxylic acids and ester to alcohols, two steps must occur: hydrogenation of the C=O bond followed by hydrogenolysis of one of the C-O bonds.⁴¹ However, the reaction temperature in this work is too low to overcome the C-O bond cleavage barrier. This was shown previously on RuMoP catalyst where the catalyst could not cleave C-O bond in cyclohexanol at less than 225°C.²⁵

Lastly, RuMoP was inactive for benzonitrile hydrogenation at the reaction condition of 125°C and 4.1 MPa H₂. However, another bimetallic phosphide, FeMoP, was shown to be active for benzonitrile reduction at 400°C to form benzylamine and toluene.⁴² Thus, the hydrogenation of benzonitrile was examined at a higher temperature of 400°C using 0.02 M of benzonitrile in n-decane as a solvent to keep the reaction in the liquid phase in the batch reactor. At 80% conversion of benzonitrile, the selectivity of the reaction was 63% benzylamine, 27% toluene, and 10% methylcyclohexane, and provides evidence that the nitrile group can be reduced at higher reaction temperature, although other side reactions are also present.⁴²⁻⁴³

4.3.3 Aromatics possessing electron donating substituents

The effects of electron donating groups were investigated through the hydrogenation of phenol, anisole, and toluene, which contain hydroxyl, ether, and methyl groups, respectively (Scheme 1g-i). The initial assessment of these reactions was performed in a flow reactor with the same reaction conditions as the other substrates (0.02 M reactant in isopropanol, 125°C, 4.1 MPa H₂). However, no reaction was observed due to the limitation of the flow reactor bed size. Therefore, a batch reactor was used to allow for longer reaction time.

Figure 4.4 summarizes the reaction results for phenol, anisole, and toluene hydrogenation represented as black squares, red circles, and blue triangles, respectively. The first three points were unquantifiable due to the small peak areas lower than the external calibration. The first quantifiable peak was

observed after 60 mins of reaction time. For all three reactions, the selectivity of the reaction was dominated (99%) by ring hydrogenation products. However, the conversion can be considered low compared to the substrates with electron withdrawing groups. The low conversion could possibly indicate preferential binding between the lone pair electrons in the solvent (isopropanol) in comparison to the π -electrons in the aromatic rings. Although phenol and anisole both have lone pair of electrons, electron density is donated to the aromatic ring, resulting in an alternative binding configuration with the Lewis acidic surface. A study on electron charge distribution on aromatics showed that the charge of the carbon in the phenyl ring increased from -0.037e to -0.100e, -0.131e, and -0.115e on the two ortho and para positions in phenol respectively.⁴⁴ The change in charge distribution shows electron donation from the hydroxy group in phenol. Nevertheless, the most electron rich atom in phenol is the hydroxyl O with charge of -0.686e, which suggests that the lone pair electrons could also bind to the electron deficient sites, but the conditions are not sufficient for C-O bond cleavage.^{25, 42, 44} The low conversion could possibly indicate preferential binding between the lone pair electrons in the solvent (isopropanol) in comparison to the π -electrons in the aromatic rings. Although phenol and anisole both have lone pair of electrons, electron density is donated to the aromatic ring, resulting in an alternative binding configuration with the Lewis acidic surface. Other noble metal catalysts such as Pd, Pt, and Ru are also shown to hydrogenate the aromatic rings for phenol hydrogenation reactions to

form cyclohexanone and cyclohexanol.⁴⁵⁻⁴⁸ These catalysts can be manipulated by changing the support material to obtain C-O bond cleavage products.⁴⁶

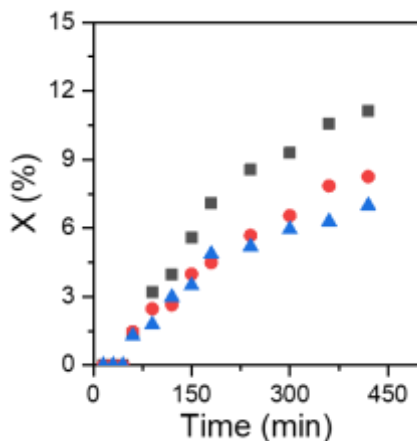


Figure 4.4. Conversion of phenol (black square), anisole (red circle), and toluene (blue triangle) hydrogenation reactions.

The hydrogenation of phenol to cyclohexanol can occur through cyclohexenol formation that isomerizes quickly into cyclohexanone.⁴⁵ The cyclohexanone is further hydrogenated into cyclohexanol. This pathway is often observed when the aromatic ring adsorbs planar on the surface, which is discussed more in the following section.⁴⁹⁻⁵⁰ However, in the reaction system, no cyclohexanone was observed. The cyclohexanol formation would imply that the interaction between phenol and the surface is through the aromatic ring and not through the lone pair of the hydroxyl O.

4.3.4 Substrates possessing both electron withdrawing and donating groups

Based on the results presented in the previous two sections, substrates containing multiple functionalities were studied to observe any competition for surface reactivity between the two groups. The first substrate studied was terephthalaldehyde (Scheme 1j), which contains two aldehyde groups in the para position of the aromatic ring. In this experiment, we were interested in understanding how RuMoP would interact with a molecule with the two aldehyde groups and if it would reduce only one of the aldehyde groups. Figure 4.5a shows the reaction results from terephthalaldehyde hydrogenation in the flow reactor where the conversion is represented in black, selectivity to p-hydroxymethylbenzaldehyde in red, and p-benzenemethanol in blue. A W/F study shows that 100% conversion can be achieved at longer residence times. However, the selectivity cannot be controlled to only one aldehyde group. Ultimately, both of the aldehyde groups are hydrogenated to form primarily p-benzenemethanol.

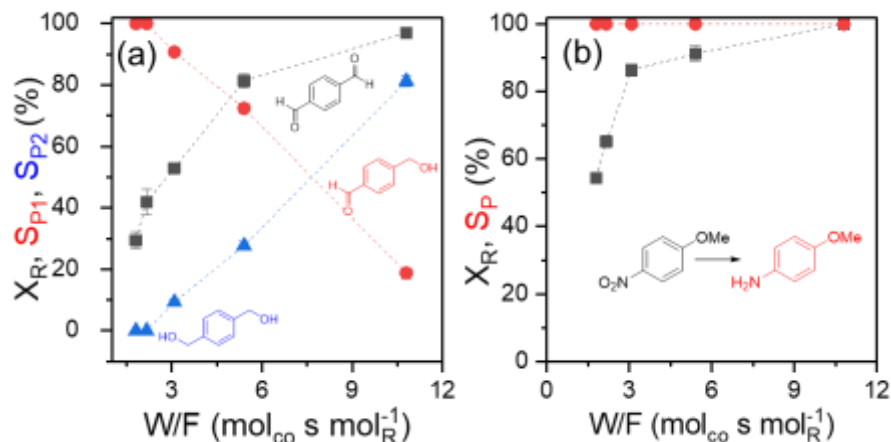


Figure 4.5. Conversion (black) and product selectivity (red, blue) for hydrogenation of (a) p-nitroanisole and (b) terephthalaldehyde as a function of W/F.

Additionally, the hydrogenation of substrates containing both an electron donating and an electron withdrawing group (i.e. p-nitroanisole) was also studied (Scheme 1k). The reaction result for p-nitroanisole hydrogenation is summarized in Figure 4.5b where the conversion is represented in black and the selectivity to p-methoxyaniline is in red. Indeed, the hydrogenation selectivity was targeted to the electron withdrawing group to form p-methoxyaniline. At 100% conversion, the selectivity is unaffected and forms only p-methoxyaniline. Although both -NH₂ and -OCH₃ are electron donating groups, the ring hydrogenation product is not observed. Other Ru-based catalysts such bimetallic RuM (*M* = Sn, Pb, Ga, Mo, W, Re) have also been studied for nitrobenzene hydrogenation in the presence of other functionalities.^{18, 51-52} In these studies, the selectivity towards nitro group reduction with Ru is improved with the addition of another metal, with some reports showing >99% selectivity to amine formation. As previously mentioned,

electronic effects associated with alloying provide an alternative route to control the catalytic properties.

To investigate the selectivity towards the electron withdrawing group, a set of DRIFTS experiments were performed using various adsorbates with nitro or methoxy functionalities. The purpose of the experiments was to observe the adsorption mode of the nitro group and the methoxy group, respectively. The first substrate used was nitrobenzene (Figure 4.6a). After desorption of physisorbed nitrobenzene under a flow of N_2 , two peaks remain at 1526 cm^{-1} for the asymmetric $\nu_{as}(\text{NO}_2)$ and 1349 cm^{-1} for the symmetric $\nu_s(\text{NO}_2)$ mode.^{6, 53} The peak positions are downshifted from the $\nu_{as}(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ in gaseous nitrobenzene at 1548 cm^{-1} and 1360 cm^{-1} , respectively.⁵⁴ The downshift in the peak positions is attributed to surface adsorption. During saturation, a feature was observed at 1448 cm^{-1} , which is an indication of the 19a type aromatic ring vibration, but this feature disappeared after N_2 purging.⁵⁵⁻⁵⁶ Since the ring vibration was not observed after purging, nitrobenzene primarily interacts with the catalytic surface through the $-\text{NO}_2$ interaction as evident by the appearance of symmetric and asymmetric features of $-\text{NO}_2$.

Anisole adsorption experiments yield two resolved features (Figure 4.6b) at 1606 cm^{-1} and 1447 cm^{-1} , which correspond to the $\nu(\text{CC}_{\text{ring}})$ vibration 8a mode and the $\delta_{as}(\text{CH}_3)$ mode, respectively.⁵⁷⁻⁵⁸ A small peak at 1489 cm^{-1} is also observed for the $\nu(\text{CC}_{\text{ring}})$ 19a vibration mode. The $\nu(\text{CO})$ band at $\sim 1498\text{ cm}^{-1}$ and $\sim 1295\text{ cm}^{-1}$ are absent, which indicates the absence of O-surface interactions.⁵⁸ This observation agrees with the reaction results where the

hydrogenation occurs primarily in the aromatic ring.⁴⁹ To investigate the competition between anisole adsorption and nitrobenzene, a physical mixture of anisole and nitrobenzene was chemisorbed on the surface to elucidate the dominate adsorption modes.⁶ When a 1:1 molar ratio of nitrobenzene and anisole were introduced into the system, features from both nitrobenzene and anisole were observed (Figure 4.6c). Therefore, simultaneous adsorption is possible; however, this result does not provide preferential adsorption between the functionalities and the surface.

The adsorption of p-nitroanisole was also observed via DRIFTS. Because p-nitroanisole is a solid, isopropanol is used to dissolve p-nitroanisole. The features associated with isopropanol adsorption include peaks in the 1445 cm^{-1} region that correspond to $\delta_{\text{as}}(\text{CH}_3)$ similar to one observed in anisole.⁵⁹⁻⁶⁰ Additionally, the 1608 cm^{-1} vibration was assigned to a C=C vibration that is similar to the observed C=C vibration in isopropanol oxidation to acetone through an enol intermediate.⁶¹⁻⁶² This C=C bond is observed when the hydroxyl O on the isopropanol is adsorbed to the active sites and form a pseudo C=C bond.⁶¹ This result indicates that the hydroxyl O from isopropanol can interact with the active sites on the surface. After dissolving p-nitroanisole with isopropanol, the mixture was placed in the N₂ bubbler. Interestingly, more features were observed in this adsorption in comparison to the physical mixture of nitrobenzene and anisole (Figure 4.6e). Features at 1600 cm^{-1} and 1447 cm^{-1} are associated with either isopropanol or anisole; and the contribution from the two adsorbates cannot be deconvoluted accurately. Peaks at 1505 and 1335 cm^{-1} are assigned to the -NO₂.

The new feature at 1490 cm^{-1} is assigned to the shifted $\nu(\text{CC}_{\text{ring}})$ from anisole. The NO_2 adsorption was shifted to a lower wavenumber, which suggests a weaker bond due to the donation from the methoxy group to the aromatic ring that can further stabilize the $-\text{NO}_2$ group. The electron donation causes the $-\text{NO}_2$ to be more electron rich, which favors adsorption to the electron deficient sites and weaken the N-O bond for subsequent reduction. Furthermore, the contribution from the H_2 was also studied with DRIFTS. The same experiment with isopropanol and p-nitroanisole was repeated, but instead of N_2 , the flow was switched to H_2 . After 10 mins, the spectrum in Figure 4.6f was observed. One major peak at 1910 cm^{-1} was observed and associated to the 19a vibration from aniline, which indicated that the reaction has proceeded and the $-\text{NO}_2$ was converted into $-\text{NH}_2$ with no additional observation of other surface intermediates. However, the adsorption on nitrobenzene in the presence of H_2 was also studied (Figure 4.6g). The spectrum provided new features at 1495 and 1304 cm^{-1} that correspond to the 19a and 14 vibration modes of phenylhydroxylamine, which is a reaction intermediate between nitrobenzene and aniline.^{7, 53} The presence of this reaction intermediates implies that nitrobenzene is directly reduced to aniline

instead of proceeding through the condensation route with azo compound formation.⁷

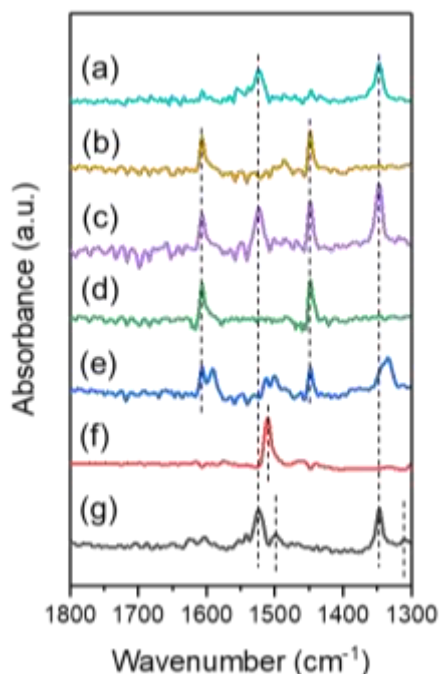


Figure 4.6. DRIFT spectra of chemisorbed (a) nitrobenzene, (b) anisole, (c) 1:1 molar ratio of nitrobenzene: anisole, (d) isopropanol, (e) isopropanol + p-nitroanisole, (f), isopropanol + p-nitroanisole + H₂, and (g) nitrobenzene + H₂.

4.3.5 Solvent effects

Isopropanol is a well-known H-donator solvent. However, within this work, isopropanol cannot be solely the H-donor which is evident by the low conversion in the absence of H₂. According to our observation, the substrates with electron donating groups tend to have lower conversion in comparison to the electron withdrawing groups, which could indicate more difficult adsorption of the aromatic ring. The aromatic ring adsorption could be further hindered from the presence of the lone pair in isopropanol that competes for the adsorption sites as shown in our DRIFTS experiments. To observe this competition, n-decane was used as a

solvent to avoid adsorption competition with the substrates. As shown in Figure 4.7, the conversion was measured as a function of time for reactions performed in a batch reactor for the hydrogenation of phenol (circle) and anisole (square). When n-decane was used as a solvent, an apparent improvement in conversion was observed as shown in Figure 4.7. At 420 min, the conversion was almost tripled with n-decane as the solvent in comparison to isopropanol. Similarly, anisole conversion was almost tripled when the solvent was switched to n-decane (red square). These results support the notion that competitive adsorption between the lone pair in isopropanol and the aromatic ring can influence the reactivity, and they also suggest that adsorption of isopropanol is more favorable than adsorption of the aromatic ring due the lower conversion observed in an isopropanol media. A similar observation was reported where the conversion of phenol increases in hydrocarbon solvents such as hexane in comparison to other solvents (i.e. alcohols, acetone, tetrahydrofuran, and ethyl acetate).⁶³⁻⁶⁵

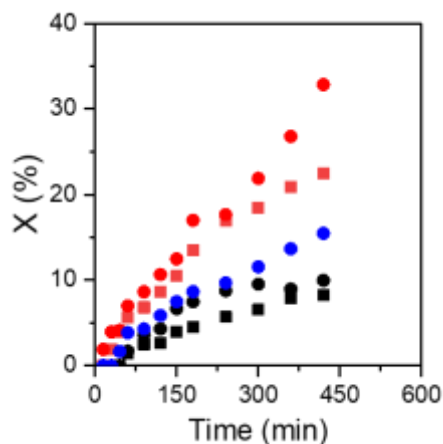


Figure 4.7. Solvent effects observed for phenol (circle) and anisole (square) hydrogenation in IPA (black) and n-decane (red) at 125°C and 150°C (blue) with RuMoP.

4.4 Conclusion

In summary, the catalytic hydrogenation performance of RuMoP was evaluated with aromatics containing electron withdrawing groups, electron donating groups, and molecules containing both types of substituents. The bimetallic RuMoP catalyst can hydrogenate benzaldehyde and benzophenone to produce 1° and 2° alcohols, respectively, with 99% selectivity. Additionally, nitrobenzene is selectively reduced to aniline with 99% selectivity using RuMoP as a catalyst. Using DRIFTS, nitrobenzene adsorption in the presence of H₂ shows this reduction occurs through a direct pathway instead of a condensation route. Hydrogenation of aromatics with electron donating groups such as phenol, anisole, and toluene yield 99% selectivity to ring hydrogenation to produce cyclohexanol, methoxycyclohexane, and methyl cyclohexane, hydrogenating the electron-dense portion of the substrate. This is supported by the presence of

Lewis acid sites in RuMoP, probed by pyridine adsorption in DRIFTS, which is likely to surface site participating in the hydrogenation reaction. The reaction results suggest the Lewis acid sites interact with part of substrates with higher electron density. In the case of aromatics with electron withdrawing groups, the substrate interaction occurs on the functional groups. On the contrary, aromatics with electron donating substituents interacts primarily from the aromatic ring. Lone pair to surface interaction was found to be more favorable than π -electrons of the aromatic ring on RuMoP surface.

4.5 References

1. Blaser, H.-U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M., Selective hydrogenation for fine chemicals: recent trends and new developments. *Adv. Synth. Catal.* **2003**, 345 (1-2), 103-151.
2. Ono, N., *The nitro group in organic synthesis*. New York : Wiley-VCH: New York, 2001.
3. Gao, R. J.; Pan, L.; Wang, H. W.; Zhang, X. W.; Wang, L.; Zou, J. J., Ultradispersed nickel phosphide on phosphorus-doped carbon with tailored d-band center for efficient and chemoselective hydrogenation of nitroarenes. *ACS Catal.* **2018**, 8 (9), 8420-8429.
4. Dimitriou, E.; Jones, R. H.; Pritchard, R. G.; Miller, G. J.; O'Brien, M., Gas-liquid flow hydrogenation of nitroarenes: Efficient access to a pharmaceutically relevant pyrrolobenzo[1,4]diazepine scaffold. *Tetrahedron* **2018**, 74 (47), 6795-6803.
5. Khilnani, V. L.; Chandalia, S. B., Selective hydrogenation. I. para-chloronitrobenzene to para-chloroaniline platinum on carbon as catalyst. *Org. Process Res. Dev.* **2001**, 5 (3), 257-262.
6. Boronat, M.; Concepcion, P.; Corma, A.; Gonzalez, S.; Illas, F.; Serna, P., A molecular mechanism for the chemoselective hydrogenation of substituted nitroaromatics with nanoparticles of gold on TiO₂ catalysts: A cooperative effect between gold and the support. *J. Am. Chem. Soc.* **2007**, 129 (51), 16230-16237.

7. Corma, A.; Concepcion, P.; Serna, P., A different reaction pathway for the reduction of aromatic nitro compounds on gold catalysts. *Angew. Chem. Int. Edit.* **2007**, 46 (38), 7266-7269.
8. Hicks, J. C., Advances in C-O Bond Transformations in Lignin-Derived Compounds for Biofuels Production. *J. Phys. Chem. Lett.* **2011**, 2 (18), 2280-2287.
9. Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A., Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chem. Soc. Rev.* **2012**, 41 (24), 8075-8098.
10. Bridgwater, A. V., Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, 38, 68-94.
11. McEwan, L.; Julius, M.; Roberts, S.; Fletcher, J. C. Q., A review of the use of gold catalysts in selective hydrogenation reactions. *Gold Bull.* **2010**, 43 (4), 298-306.
12. Maki-Arvela, P.; Hajek, J.; Salmi, T.; Murzin, D. Y., Chemoselective hydrogenation of carbonyl compounds over heterogeneous catalysts. *Appl. Catal. A* **2005**, 292, 1-49.
13. Wang, Y.; Yao, J.; Li, H. R.; Su, D. S.; Antonietti, M., Highly selective hydrogenation of phenol and derivatives over a Pd@carbon nitride catalyst in aqueous media. *J. Am. Chem. Soc.* **2011**, 133 (8), 2362-2365.
14. Gu, J.; Zhang, Z. Y.; Hu, P.; Ding, L. P.; Xue, N. H.; Peng, L. M.; Guo, X. F.; Lin, M.; Ding, W. P., Platinum nanoparticles encapsulated in MFI zeolite crystals by a two-step dry gel conversion method as a highly selective hydrogenation catalyst. *ACS Catal.* **2015**, 5 (11), 6893-6901.
15. Wei, H. S.; Liu, X. Y.; Wang, A. Q.; Zhang, L. L.; Qiao, B. T.; Yang, X. F.; Huang, Y. Q.; Miao, S.; Liu, J. Y.; Zhang, T., FeOx-supported platinum single-atom and pseudo-single-atom catalysts for chemoselective hydrogenation of functionalized nitroarenes. *Nat. Commun.* **2014**, 5.
16. Kluson, P.; Cervený, L., Selective Hydrogenation over Ruthenium Catalysts. *Appl. Catal. A* **1995**, 128 (1), 13-31.
17. Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D., Solvent-free, low-temperature, selective hydrogenation of polyenes using a bimetallic nanoparticle Ru-Sn catalyst. *Angew. Chem. Int. Edit.* **2001**, 40 (7), 1211.
18. Tamura, M.; Yuasa, N.; Nakagawa, Y.; Tomishige, K., Selective hydrogenation of nitroarenes to aminoarenes using a MoOx-modified

- Ru/SiO₂ catalyst under mild conditions. *Chem. Commun.* **2017**, 53 (23), 3377-3380.
19. Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D., Heterogeneous catalytic transfer hydrogenation and its relation to other methods for reduction of organic compounds. *Chem. Rev.* **1985**, 85 (2), 129-170.
 20. Nozaki, F.; Tokumi, M., Hydrogenation Activity of Metal Phosphides and Promoting Effect of Oxygen. *J. Catal.* **1983**, 79 (1), 207-210.
 21. Nozaki, F.; Kitoh, T.; Sodesawa, T., Promoting Effect of Oxygen for Hydrogenation of Butadiene over Ni₂P Catalyst. *J. Catal.* **1980**, 62 (2), 286-293.
 22. Wang, H.; Shu, Y. Y.; Zheng, M. Y.; Zhang, T., Selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde over SiO₂ supported nickel phosphide catalysts. *Catal. Lett.* **2008**, 124 (3-4), 219-225.
 23. Liu, K.; Wang, Y.; Chen, P.; Zhong, W. B.; Liu, Q. Z.; Li, M. F.; Wang, Y. D.; Wang, W. W.; Lu, Z. T.; Wang, D., Noncrystalline nickel phosphide decorated poly(vinyl alcohol-co-ethylene) nanofibrous membrane for catalytic hydrogenation of p-nitrophenol. *Appl. Catal. B* **2016**, 196, 223-231.
 24. Rensel, D. J.; Rouvimov, S.; Gin, M. E.; Hicks, J. C., Highly selective bimetallic FeMoP catalyst for C-O bond cleavage of aryl ethers. *J. Catal.* **2013**, 305, 256-263.
 25. Bonita, Y.; Hicks, J. C., Periodic trends from metal substitution in bimetallic Mo-based phosphides for hydrodeoxygenation and hydrogenation reactions. *J. Phys. Chem. C* **2018**, 122 (25), 13322-13332.
 26. Jain, V.; Bonita, Y.; Brown, A.; Taconi, A.; Hicks, J. C.; Rai, N., Mechanistic insights into hydrodeoxygenation of phenol on bimetallic phosphide catalysts. *Catal. Sci. Technol.* **2018**, 8 (16), 4083-4096.
 27. Corro, G.; Gomez, R., Carbon-monoxide adsorption and hydrogen-oxygen titration on Ru-Al₂O₃. *React. Kinet. Catal. L.* **1979**, 12 (2), 145-150.
 28. Chakraborty, B.; Viswanathan, B., Surface acidity of MCM-41 by in situ IR studies of pyridine adsorption. *Catal. Today* **1999**, 49 (1), 253-260.
 29. Zaki, M. I.; Hasan, M. A.; Al-Sagheer, F. A.; Pasupulety, L., In situ FTIR spectra of pyridine adsorbed on SiO₂-Al₂O₃, TiO₂, ZrO₂ and CeO₂: general considerations for the identification of acid sites on surfaces of finely divided metal oxides. *Colloid Surf., A* **2001**, 190 (3), 261-274.

30. Basila, M. R.; Kantner, T. R.; Rhee, K. H., The nature of the acidic sites on a silica-alumina. Characterization by infrared spectroscopic studies of trimethylamine and pyridine chemisorption. *J. Phys. Chem.* **1964**, 68 (11), 3197-3207.
31. Layman, K. A.; Ivey, M. M.; Hemminger, J. C., Pyridine adsorption and acid/base complex formation on ultrathin films of γ -Al₂O₃ on NiAl(100). *J. Phys. Chem. B* **2003**, 107 (33), 8538-8546.
32. Lee, Y. K.; Oyama, S. T., Bifunctional nature of a SiO₂-supported Ni₂P catalyst for hydrotreating: EXAFS and FTIR studies. *J. Catal.* **2006**, 239 (2), 376-389.
33. Barzetti, T.; Selli, E.; Moscotti, D.; Forni, L., Pyridine and ammonia as probes for FTIR analysis of solid acid catalysts. *J Chem Soc Faraday T* **1996**, 92 (8), 1401-1407.
34. Parry, E. P., An infrared study of pyridine adsorbed on acidic solids characterization of surface acidity. *J. Catal.* **1963**, 2 (5), 371-379.
35. Hadjiloizou, G. C.; Butt, J. B.; Dranoff, J. S., Pyridine hydrogenation and piperidine hydrogenolysis on a commercial hydrocracking catalyst I. Reaction and deactivation kinetics. *J. Catal.* **1991**, 131 (2), 545-572.
36. Sampath, A.; Chang, S. A.; Flaherty, D. W., Catalytic hydrogen transfer and decarbonylation of aromatic aldehydes on Ru and Ru phosphide model catalysts. *The Journal of Physical Chemistry C* **2018**, 122 (41), 23600-23609.
37. Bowker, R. H.; Smith, M. C.; Pease, M. L.; Slenkamp, K. M.; Kovarik, L.; Bussell, M. E., Synthesis and hydrodeoxygenation properties of ruthenium phosphide catalysts. *ACS Catal.* **2011**, 1 (8), 917-922.
38. Singh, U. K.; Vannice, M. A., Liquid-phase citral hydrogenation over SiO₂-supported group VIII metals. *J. Catal.* **2001**, 199 (1), 73-84.
39. O'Driscoll, A.; Curtin, T.; Hernandez, W. Y.; Van Der Voort, P.; Leahy, J. J., Hydrogenation of furfural with a Pt-Sn catalyst: the suitability to sustainable industrial application. *Org Process Res Dev* **2016**, 20 (11), 1917-1929.
40. Plomp, A. J.; Vuori, H.; Krause, A. O. I.; de Jong, K. P.; Bitter, J. H., Particle size effects for carbon nanofiber supported platinum and ruthenium catalysts for the selective hydrogenation of cinnamaldehyde. *Applied Catalysis A: General* **2008**, 351 (1), 9-15.
41. Pritchard, J.; Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A., Heterogeneous and homogeneous catalysis for the hydrogenation of

carboxylic acid derivatives: history, advances and future directions. *Chem. Soc. Rev.* **2015**, *44* (11), 3808-3833.

42. Rensel, D. J.; Kim, J.; Jain, V.; Bonita, Y.; Rai, N.; Hicks, J. C., Composition-directed $\text{Fe}_x\text{Mo}_{2-x}\text{P}$ bimetallic catalysts for hydrodeoxygenation reactions. *Catal. Sci. Technol.* **2017**, *7*, 1857-1867.
43. Yan, K.; Chen, A. C., Selective hydrogenation of furfural and levulinic acid to biofuels on the ecofriendly Cu-Fe catalyst. *Fuel* **2014**, *115*, 101-108.
44. Misiaszek, T.; Szostak, M. M., Atomic charge distribution in 4-isopropylphenol molecule derived from atomic polar tensors. *J. Molec. Struct.* **2000**, *526* (1), 303-308.
45. Liu, H. Z.; Jiang, T.; Han, B. X.; Liang, S. G.; Zhou, Y. X., Selective phenol hydrogenation to cyclohexanone over a dual supported Pd-Lewis acid catalyst. *Science* **2009**, *326* (5957), 1250-1252.
46. Newman, C.; Zhou, X.; Goundie, B.; Ghampson, I. T.; Pollock, R. A.; Ross, Z.; Wheeler, M. C.; Meulenbergh, R. W.; Austin, R. N.; Frederick, B. G., Effects of support identity and metal dispersion in supported ruthenium hydrodeoxygenation catalysts. *Appl. Catal. A* **2014**, *477*, 64-74.
47. Li, Z.; Garedew, M.; Lam, C. H.; Jackson, J. E.; Miller, D. J.; Saffron, C. M., Mild electrocatalytic hydrogenation and hydrodeoxygenation of bio-oil derived phenolic compounds using ruthenium supported on activated carbon cloth. *Green Chem.* **2012**, *14* (9), 2540-2549.
48. Ohta, H.; Kobayashi, H.; Hara, K.; Fukuoka, A., Hydrodeoxygenation of phenols as lignin models under acid-free conditions with carbon-supported platinum catalysts. *Chem. Commun.* **2011**, *47* (44), 12209-12211.
49. Zhong, J. W.; Chen, J. Z.; Chen, L. M., Selective hydrogenation of phenol and related derivatives. *Catal. Sci. Technol.* **2014**, *4* (10), 3555-3569.
50. Taylor, D. R.; Ludlum, K. H., Structure and orientation of phenols chemisorbed on gamma-alumina. *J. Phys. Chem.* **1972**, *76* (20).
51. Coq, B.; Figueras, F., Geometric and Electronic Effects in the Conversion of Methylcyclopentane on Pt-Sn Catalysts. *J Mol Catal* **1984**, *25* (1-3), 87-98.
52. Chary, K. V. R.; Srikanth, C. S., Selective hydrogenation of nitrobenzene to aniline over Ru/SBA-15 catalysts. *Catal. Lett.* **2009**, *128* (1), 164-170.
53. Richner, G.; van Bokhoven, J. A.; Neuhold, Y. M.; Makosch, M.; Hungerbuhler, K., In situ infrared monitoring of the solid/liquid catalyst

- interface during the three-phase hydrogenation of nitrobenzene over nanosized Au on TiO₂. *Phys. Chem. Chem. Phys.* **2011**, 13 (27), 12463-12471.
54. Varsányi, G.; Holly, S.; Imre, L., Some characteristic vibration patterns of the organic nitro group. *Spectrochimica Acta Part A: Molecular Spectroscopy* **1967**, 23 (5), 1205-1210.
 55. Clavijo-Campos, R. E.; Weiss-López, B., Phase dependence of the IR spectra of nitrobenzene *Spectrosc. Lett.* **1990**, 23 (1), 137-145.
 56. Meijers, S.; Ponec, V., Infrared spectroscopic study of the adsorption of nitro compounds and amines on cobalt oxide. *J. Catal.* **1994**, 149 (2), 307-316.
 57. Gemechu, A. S.; Hoffmann, L. J. H.; Marquardt, S.; Eisenhardt, C. G.; Baumgartel, H.; Chelli, R.; Cardini, G.; Califano, S., The absorption spectrum of anisole and the anisole/CO₂ 1 : 1-cluster. The influence of intermolecular interaction on intramolecular vibrations. *Z. Phys. Chem.* **2004**, 218 (1), 123-153.
 58. Popov, A.; Kondratieva, E.; Gilson, J. P.; Mariey, L.; Travert, A.; Mauge, F., IR study of the interaction of phenol with oxides and sulfided CoMo catalysts for bio-fuel hydrodeoxygenation. *Catal. Today* **2011**, 172 (1), 132-135.
 59. Carriazo, D.; Martin, C.; Rives, V., An FT-IR study of the adsorption of isopropanol on calcined layered double hydroxides containing isopolyniobate. *Catal. Today* **2007**, 126 (1-2), 153-161.
 60. Martinez-Ramirez, Z.; Gonzalez-Calderon, J. A.; Almendarez-Camarillo, A.; Fierro-Gonzalez, J. C., Adsorption and dehydrogenation of 2-propanol on the surface of gamma-Al₂O₃-supported gold. *Surf. Sci.* **2012**, 606 (15-16), 1167-1172.
 61. Li, S. Z.; Wen, M.; Chen, H.; Ni, Z. L.; Xu, J.; Shen, J. Y., Amination of isopropanol to isopropylamine over a highly basic and active Ni/LaAlSiO catalyst. *J. Catal.* **2017**, 350, 141-148.
 62. Barakat, C.; Gravejat, P.; Guaitella, O.; Thevenet, F.; Rousseau, A., Oxidation of isopropanol and acetone adsorbed on TiO₂ under plasma generated ozone flow: Gas phase and adsorbed species monitoring. *Appl. Catal. B* **2014**, 147, 302-313.
 63. Feng, G.; Liu, Z.; Chen, P.; Lou, H., Influence of solvent on upgrading of phenolic compounds in pyrolysis bio-oil. *RSC Adv.* **2014**, 4 (91), 49924-49929.

64. Takagi, H.; Isoda, T.; Kusakabe, K.; Morooka, S., Effects of solvents on the hydrogenation of mono-aromatic compounds using noble-metal catalysts. *Energ. Fuel* **1999**, 13 (6), 1191-1196.
65. Wang, X.; Rinaldi, R., Solvent effects on the hydrogenolysis of diphenyl ether with Raney nickel and their Implications for the conversion of lignin. *ChemSusChem* **2012**, 5 (8), 1455-1466.

CHAPTER 5

DIRECT SYNTHESIS OF FURFURYL ALCOHOL FROM FURFURAL: CATALYTIC PERFORMANCE OF MONOMETALLIC AND BIMETALLIC MO AND RU PHOSPHIDES[†]

5.1 Introduction

As mentioned in Chapter 1, furfuryl alcohol (FOL) is an important chemical intermediate with a variety of applications in resins, lubricants, fragrances, flavorings, and lysine production.¹⁻⁴ In current furfuryl alcohol production, Cu-chromite (CuCr_2O_4) is used as a catalyst to selectively hydrogenate furfural (FAL), a platform molecule that is also derived from lignocellulosic biomass.⁵⁻⁶ Although Cu-chromite achieves high selectivity to FOL (>99%) at complete conversion, two primary issues have been identified with this catalytic system: (1) environmental concerns exist with the disposal of spent Cu-chromite catalysts,⁵ and (2) Cu-chromite suffers from rapid deactivation due to coke formation or via a change in the Cu oxidation state during reaction.^{5, 7-8}

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A variety of alternative Cu-based catalysts have been studied in significant detail, including Cu/C, Cu/ZnO, Cu-Ni, Cu-Co, and Cu-Fe.⁹⁻¹⁴ In bimetallic Cu-Fe and Cu-Ni, structural and electronic effects from well-distributed metal atoms or charge transfer between the metals contributed to variations in the catalytic performance for FAL hydrogenation.⁹⁻¹⁰ As a result, a shift in the product distribution was observed where methylfuran (MF) was the dominant product.⁹⁻¹⁰ Noble metal-based catalysts such as Pt, Rh, Pd, and Ru have also been reported as highly active catalysts for FAL hydrogenation.¹⁵ Nevertheless, the main hydrogenation product observed was tetrahydrofurfuryl alcohol (THFA), which was formed via FOL ring hydrogenation. Efforts to tune the selectivity of noble metal catalysts have included pairing the noble metal with a less reactive metal such as Sn, where the incorporation of Sn can either improve the FAL selectivity when paired with Ru or increase the reactivity when paired with Pt.¹⁶⁻¹⁷ Other metals such as Mo, Mn, and Fe have also been shown to enhance the selectivity to FAL in Pt-based materials.¹⁸

Noble metal based phosphides such as Ru_xP , Rh_2P , and Pd_3P were able to deoxygenate biomass-derived molecules,¹⁹⁻²¹ with MoP and Ni_2P as potential catalysts for vapor phase furfural hydrogenation to form methylfuran.²² We have recently reported the low temperature hydrogenation ability of noble metal-based bimetallic $Ru_{1.0}Mo_{1.0}P$ for hydrogenation of various aromatic functionalities such as benzaldehyde to benzyl alcohol.²³⁻

²⁴ The Lewis acidic nature of Ru_{1.0}Mo_{1.0}P was responsible for the reduction of the aldehyde and is a reasonable catalyst for the selective production of FOL from FAL.²⁴

Herein, we report a detailed comparison of monometallic MoP, Mo₃P, RuP, Ru₂P phosphides and bimetallic Ru_xMo_{2-x}P phosphides for FAL hydrogenation. A series of experiments and simulations were used to determine the following: (1) if transition metal phosphides were capable of performing selective hydrogenation of FAL to FOL, (2) if an enhancement in catalytic activity and selectivity is observed with bimetallic materials, and (3) the catalytic consequences of changing the metal ratio in Ru_xMo_{2-x}P. We close this manuscript with recycle studies of high performing bimetallic catalysts.²⁵

5.2 Experimental

5.2.1 Materials

Citric acid monohydrate (Amresco, 99%), (NH₄)₆Mo₇O₂₄·4H₂O (Alfa Aesar, 99%), RuCl₃·xH₂O (Oakwood Chemicals, 90%), (NH₄)₂HPO₄ (Amresco, 98.6%), furfural (Sigma Aldrich, 99.5%), furfuryl alcohol (TCI Chemicals), 2-methyl furan (TCI Chemicals, 99%), tetrahydrofurfuryl alcohol (Alfa Aesar, 99%), 2-propanol (J.T. Baker, 99%), 5% Ru/Al₂O₃ (Riogen).

All of the gases are purchased from Airgas: H₂ (99.999%), N₂ (99.999%), 1%O₂/He, 30%CO/He, 2%NH₃/He.

5.2.2 Catalyst synthesis and characterization

The synthesized materials were characterized using various methods. A Bruker powder x-ray diffractometer (XRD) with a Cu-K α source was used to confirm the crystal structures of the materials. Rietveld refinement was performed using FullProf Suite software. A Si (111) standard was added, and the corresponding peak was shifted to 28.44° 2 θ . The Brunauer-Emmett-Teller (BET) surface area was measured with a Quantachrome Nova 2200e with N₂ at 77 K. A Micromeritics Chemisorb 2750 unit equipped with a thermal conductivity detector (TCD) was used to quantify the CO-accessible sites. For CO-pulse chemisorption experiments, the samples were pretreated under 20 mL/min of H₂ flow at 400°C with a 10°C/min ramp rate for 2 h followed by 20 mL/min of He flow at the same temperature for 1.5 h and 20 mL/min of H₂ flow at 100°C for 1 h to prevent polycarbonyl formation.²⁶ The CO-pulse was performed at 35°C with 0.1 mL injections of 30% CO in He. The amount of CO chemisorbed was quantified using an external calibration curve. The desorption was performed using a 10°C/min ramp rate to a final temperature of 450°C. Elemental analysis was done with a Perkin Elmer Optima 8000 Inductively Coupled Plasma (ICP) – Optical Emission Spectroscopy (OES) system and quantified using an external calibration.

X-Ray photoelectron spectroscopy (XPS) was used to determine the binding energies of the various catalysts. All sample preparations occurred in a N₂ glove box, and the exposure to air during sample transfer was minimized.

Elemental Ni powder was physically mixed into the sample as a standard where the Ni 2p_{3/2} peak was shifted to 852.60 eV. Asymmetric peak fitting was applied in the deconvolution of XP spectra peaks.²⁷⁻²⁹ The XP spectra in the Mo 3d region was deconvoluted into the reduced Mo 3d_{5/2} and 3d_{3/2} pair. The contribution from the oxidized species can be observed in the satellite peak that was deconvoluted into the oxidized Mo 3d_{5/2} and 3d_{3/2} pair. The low amount of oxidized species observed was attributed to the brief exposure to air during sample transfer or possibly an oxidized layer that formed during passivation. The P 2p region was deconvoluted into the reduced 2p_{3/2} and 2p_{1/2} doublet and the oxidized 2p_{3/2} and 2p_{1/2} doublet at higher binding energies. The Ru 3p region was deconvoluted into the reduced 3p_{3/2} and 3p_{1/2} doublet as well as its oxidized contributions. The Ru 3p region was used to determine the surface composition of the materials since the Ru 3d region overlaps with the C 1s peak.

X-ray absorption spectroscopy (XAS) experiments were performed at Argonne National Laboratory in the Advanced Photon Source sector 10 Insertion Device (ID) line of the Material Research Collaborative Access Team (MRCAT). Boron nitride was used to dilute the samples to obtain a sufficient signal. Approximately 10 mg of the mixture was pressed into a pellet in the sample holder. The sample was placed inside a sealed pretreatment cell, and the samples were pretreated at 450 °C under 4% of H₂ in He for 1 hr. After the cell was cooled down, the cell was sealed and placed for analysis. The

measurements were obtained under transmission mode with a 10^5 photon flux per second. WinXAS 3.1 was used to analyze the data.

A Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer equipped with a Harrick Praying Mantis diffuse reflectance high temperature reaction cell (ZnSe windows) accessory was used to study the interaction of furfural with the catalyst surface. In a typical experiment, the catalyst sample (20 mg) was loaded in the sample cup and pretreated with 30 mL/min of H_2 at $400^\circ C$ for 2 h followed by 30 mL/min of N_2 at $400^\circ C$ for 1 hour. After the pretreatment, the sample was cooled down to room temperature, and a background measurement was performed. Furfural was loaded into a glass bubbler with 30 mL of N_2 flow used as the carrier gas to saturate the sample for 30 mins at room temperature. The saturated samples were then purged with N_2 for 30 mins. The IR spectra were recorded over 1000 scans with a 1 cm^{-1} resolution with a liquid N_2 cooled mercury cadmium telluride (MCT) detector.

5.2.3 Catalyst testing

The catalytic testing was performed in a 300 mL Parr batch reactor. Based on the CO chemisorption experiments, the reactor was loaded with the same amount of catalyst in each experiment ($0.45\text{ }\mu\text{mol}$ of CO sites for each catalyst). The reaction media consisted of 40 mL of 0.1 M FAL in isopropanol with dioxane added as an internal standard unless otherwise specified. The reactor was charged with H_2 to the pressure of interest. Using a 1/16" sampler

tube installed inside the reactor, 250 μL samples were taken at various times during the reaction. The line was flushed between each sampling in order to prevent any cross contamination with previous sampling times. The reaction results were analyzed using gas chromatography – mass spectrometry (GCMS, Agilent 5975-7890) and quantified with an external calibration curve created for each reactant and product. The carbon balance for all points was >95%. The conversion and selectivity were calculated according to Equation (1) and (2) respectively where X_{FAL} is the FAL conversion, S_{FOL} is selectivity to FOL, and C_j is the concentration of the species, j.

$$X_{\text{FAL}} = 1 - \frac{C_{\text{FAL},out}}{C_{\text{FAL},in}} \quad (\text{Equation 5.1})$$

$$S_{\text{FOL}} = \frac{C_{\text{FOL}}}{C_{\text{FOL}} + C_{\text{MF}} + C_{\text{THFA}}} \quad (\text{Equation 5.2})$$

The conversion over time was fitted into a pseudo-1st order batch reactor equation (Equation 4) that was obtained from Equation 3 to extract the reaction rate constant, k_1 , for furfural hydrogenation to furfuryl alcohol.

$$\frac{dC_{\text{FAL}}}{dt} = -k_1 C_{\text{FAL}} \quad (\text{Equation 5.3})$$

$$-\ln(1 - X_{\text{FAL}}) = k_1 t \quad (\text{Equation 5.4})$$

Subsequent reactions with 0.10 M furfuryl alcohol as the substrate were performed to extract the rate constant of MF and tetrahydrofurfuryl alcohol (THFA),

denoted as k_2 and k_3 , respectively. Equation 5 was derived for parallel 1st order reactions in a batch reactor. Accordingly, a plot of $\ln(1-X_{FOL})$ against time resulted in a slope of $k_2 + k_3$.

$$C_{FOL} = C_{FAL,in} \exp(-(k_2 + k_3) t) \quad (\text{Equation 5.5})$$

The time-dependent C_{MF} and C_{THFA} values in Equation 6 and 7 were then derived. The ratio between C_{MF} and C_{THFA} resulted in Equation 8, which was plotted to obtain k_2/k_3 . Using these equations, k_2 and k_3 were determined.

$$C_{MF} = \frac{k_2 C_{FOL,in}}{k_2 + k_3} (1 - \exp(-(k_2 + k_3) t)) \quad (\text{Equation 5.6})$$

$$C_{THFA} = \frac{k_3 C_{FOL,in}}{k_2 + k_3} (1 - \exp(-(k_2 + k_3) t)) \quad (\text{Equation 5.7})$$

$$C_{MF} = \frac{k_2}{k_3} C_{THFA} \quad (\text{Equation 5.8})$$

5.2.4 Computational details

We performed plane wave periodic density functional theory (DFT)³⁰⁻³¹ calculations using Vienna *ab initio* simulation package (VASP.5.4.4).³²⁻³⁵ We used the optB88-vdW functional, which accounts for nonlocal, long-range van der Waals interactions.³⁶⁻³⁷ The core electrons are described with the projector augmented wave (PAW) method³⁸ to solve the Kohn-Sham equations.³⁹⁻⁴⁰ The energy cut-off was taken as 450 eV to ensure high precision. Total energies were calculated using a first-order

Methfessel–Paxton smearing function with a width of 0.1 eV, and the total energy was extrapolated to 0 K.⁴¹ Optimizations were carried out until the net forces acting on atoms were smaller than 0.03 eV Å⁻¹, using a total energy convergence of 1x10⁻⁵ eV. The calculations were carried out with spin polarization. For the integration of the Brillouin zone (BZ), we used a Γ -point sampling in all calculations.⁴² The partial charges on various species were derived using a Bader charge analysis.⁴³⁻⁴⁶

Crystal structures of three Ru_xMo_{2-x}P catalysts were optimized in three-dimensional periodic boundary conditions based on the cell parameters determined via XRD patterns of these catalysts. Optimized unit cell parameters in these catalysts showed a deviation of $\leq 1\%$ in comparison with those experimentally determined (Table A.3). Using these optimized cell parameters, the model phosphide surface was constructed by implementing the standard slab approach, in which a slab of finite thickness was cut out of the Ru_xMo_{2-x}P crystal at the (112) plane to expose an atomic layer that has all three types of atoms in each catalytic surface. We applied the same approach to the (210) plane for comparison between the two surfaces. The number of phosphorus atoms was maintained constant (60 atoms) for all the calculations, whereas the number of Ru and Mo atoms was governed by the stoichiometry.

The slab used for simulations consists of three layers in Ru_xMo_{2-x}P with a supercell size P (2 X 2) with a 15 Å thick vacuum layer in the z-

direction (perpendicular to the surface) to minimize interactions between neighboring image slabs. For all calculations, the bottom most layer was fixed to represent the corresponding crystal structure obtained from DFT, whereas all other atoms were allowed to relax.

The adsorption energies (denoted as E_{AD}) were calculated according to Eqn. (9), wherein $E_{ADSORBATE+SURFACE}$ is defined as the total energy of species adsorbed on the surface; $E_{SURFACE}$ is defined the total energy of surface; and $E_{ADSORBATE}$ is defined as the energy of the adsorbed species on the surface in the gas phase.

$$E_{AD} = E_{ADSORBATE+SURFACE} - E_{SURFACE} - E_{ADSORBATE} \quad (\text{Equation 5.9})$$

5.3 Result and discussion

5.3.1 Catalytic evaluation of monometallic phosphides

Four unsupported monometallic phosphides MoP, Mo₃P, RuP, and Ru₂P were synthesized using the TPR method described in detail in the supporting information. The crystal structures were confirmed using XRD (Figure A.4 and Figure A.5).

Table 5.1 summarizes the textural properties of all the phosphide catalysts used in this study as well as results from CO titrations (N_{CO}). The S_{BET} was obtained using N₂ physisorption, and the values ranged from 6.1 m²/g – 12 m²/g for all materials except for MoP (32 m²/g), which are similar

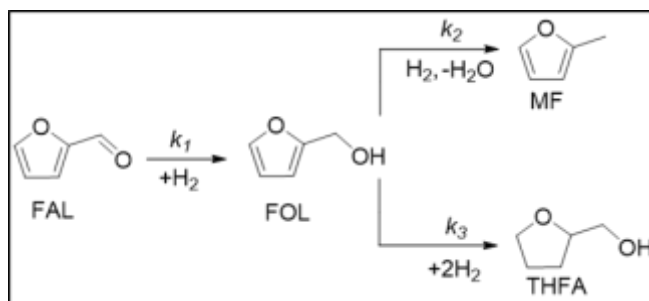
to other reports.⁴⁷⁻⁴⁹ The S_{BET} of Mo_3P was lower than MoP due to higher reduction temperature needed to synthesize Mo_3P (800°C). It is possible to vary the amount of citric acid added during synthesis to increase the surface area of the resulting materials.⁵⁰ Supporting the phosphides can improve the surface area; however, multiple phases can be formed, and the the various phosphide phases may add complexity to the evaluation of their catalytic performance.⁵¹⁻⁵² CO-pulse chemisorption was used to quantify the number of CO adsorption sites for each of the phosphide catalysts. The CO-titration results provided similar values ranging between 20-28 $\mu\text{mol/g}$ on all materials, and these values were used to standardize the experiments as well as normalize the reaction rates in some cases.

TABLE 5.1.
TEXTURAL PROPERTIES OF MO-BASED AND RU-BASED

Catalysts	S_{BET} (m^2/g)	N_{CO} ($\mu\text{mol/g}$)
MoP	32	28
Mo_3P	6.1	25
RuP	12	23
Ru_2P	10	24
$\text{Ru}_{0.8}\text{Mo}_{1.2}\text{P}$	9.2	21
$\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$	7.2	20
$\text{Ru}_{1.2}\text{Mo}_{0.8}\text{P}$	11	25

Scheme 1 represents the reaction pathways observed in this study. In the first hydrogenation step, FAL is converted into FOL with a rate

constant denoted as k_1 . To measure this rate constant, the monometallic catalysts were tested in a batch reactor with 0.10 M FAL in isopropanol at 100°C and 4.2 MPa. Using the CO chemisorption values, the catalyst loading in each experiment was maintained at 0.45 μmol of CO accessible sites for all experiments based on the invariance observed between the consumption rate of furfural with respect to the catalyst amount (Figure A.6) and prior literature suggesting CO titrated sites as the active sites for FAL hydrogenation.^{5, 16} Samples were taken throughout the reaction, and the conversion was plotted according to Equation 4 to obtain a pseudo-1st order rate constant, k_1 .



Scheme 5.1. Reaction pathway of FAL hydrogenation to produce FOL, MF, and THFA.

Several reaction mechanisms based on a Langmuir-Hinshelwood model have been proposed for FAL hydrogenation involving adsorption of both H_2 and FAL.^{11, 53-56} From these mechanisms, several rate laws have been derived in the literatures.^{11, 54-55} In each of these cases, dependence on both H_2 and FAL concentrations complicate the rate measurements.

To simplify the kinetic expression, the reaction was operated at the appropriate pressure such that the rate depended only on FAL and not H_2 . To confirm that the operating H_2 pressure was in the 0th order region, several experiments were performed at 100°C with different partial pressures of H_2 while keeping the total pressure of 4.2 MPa using N_2 as the balancing gas. The results are plotted in A.7 as $-\ln(1-X)$ against reaction time, where X is the FAL conversion. The reaction constant, k_1 , was obtained from the slope of the plot in Figure A.7 for 2.1 MPa, 3.4 MPa, 3.8 MPa, and 4.2 MPa H_2 partial pressure. The linear dependency between $-\ln(1-X)$ and reaction time observed in the plot implied a pseudo-1st order dependency in FAL concentration could be assumed. Moreover, the kinetic profiles and k_1 were statistically invariant according to the Dixon q-test (Equation S1) in experiments between 3.4 – 4.2 MPa H_2 partial pressure, which provided a suitable kinetic region to compare catalytic materials.⁵⁷

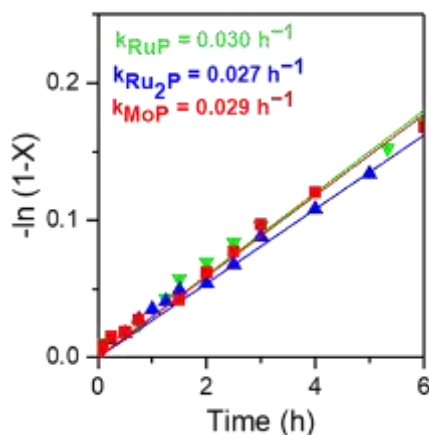


Figure 5.1. The difference in rate constant k_1 between monometallic RuP (green – $R^2 = 0.976$), Ru_2P (blue – $R^2 = 0.984$), and MoP (red – $R^2 = 0.987$).

In addition to the H₂ pressure study, the initial concentration of FAL was varied to confirm the pseudo-1st order trend initially observed. With a 4.2 MPa H₂ pressure, five initial concentrations of FAL in IPA (0.10M, 0.15M, 0.18M, and 0.25 M) were studied in a batch reactor at 100°C with real-time sampling of the reaction progress. The reaction results are plotted as -ln (1-X) versus time in Figure A.8 for all initial FAL concentrations. The linear trend observed in the plot further indicated pseudo-1st order behavior in FAL for all initial concentrations. Moreover, the k-values were extracted from the slopes to yield k₁ of 0.176 h⁻¹, 0.177 h⁻¹, 0.171 h⁻¹, and 0.174 h⁻¹ for initial concentration of 0.10 M, 0.15 M, 0.18 M, and 0.25 M, respectively. At higher FAL concentration (i.e., 0.50 M), the solubility of H₂ decreases and new reaction conditions to satisfy the pseudo-1st order model with excess H₂ in solution are required.⁵⁸ Therefore, to fulfill the pseudo-1st order assumptions, an initial concentration of 0.10 M for FAL is used throughout the experiments. At lower concentrations (0.01 M – 0.05 M), lower than unity order dependency was observed as shown in other reports for FAL hydrogenation over a Pt/C catalyst.⁵³ The rate expression can therefore be simplified to Equation 3, with k₁ representing the lumped, pseudo-1st order reaction rate constant.

Background experiments were also performed to quantify the contribution of H₂ transfer from isopropanol (solvent). After 24 h of reaction time at 4.2 MPa of N₂ pressure for proper comparison, the furfural

conversion was 1.1% with only isopropanol as the H₂ source. Therefore, these contributions were considered negligible in this study. After linearization of Equation 10, the various catalysts were studied and compared (Figure 5.1). The rate constant, k_1 , was measured as 0.030 h⁻¹, 0.027 h⁻¹, and 0.029 h⁻¹ for RuP, Ru₂P, and MoP, respectively. These rate constants were similar in magnitude for all monometallic materials. Mo₃P was also tested for this reaction, but it was inactive at temperatures tested below 125°C, which is likely due to unfavorable adsorption of the reactant as also noted by Xiao et al.⁵⁹ At much higher temperatures (>300°C), however, Mo₃P was active with ~80% selectivity to 2-(isopropoxy)methyl furan from the etherification reaction between FAL and isopropanol. This result is a possible indication of the weak (or lack of) Brønsted acidity of the phosphides, resulting in the production of the ether product.^{24, 60-62}

All active catalysts also showed a high selectivity to FOL production. At a conversion of 15%, the selectivity towards FOL was 98 ± 0.8% for MoP, while the selectivity decreased slightly to 97 ± 1.2% and 94 ± 1.3% for RuP and Ru₂P, respectively, with MF observed as the other by-product. It was apparent that MoP showed the highest selectivity towards FOL, while the highest rate constant was observed with RuP.

Subsequently, FOL was used as a reactant to determine k_2 and k_3 , which correspond to rate constants to produce MF and THFA, respectively (Scheme 1).

The constants were determined with batch reaction experiments using 0.10 M FOL in isopropanol as a reactant. Equation 5 and Equation 8 were used to extract k_2 and k_3 values simultaneously. These values were then used to model the concentration of FOL, MF, and THFA with all active monometallic catalysts. The model was plotted with the raw data for MoP, RuP, and Ru₂P in Figure 5.2a-c. From these plots, it could be seen that the model fits the raw well. The k -values are compiled in Table A.5 for comparison. The rate constants for MF formation (k_2) were 0.0035 h⁻¹, 0.0013 h⁻¹, and 0.0002 h⁻¹ for MoP, RuP, and Ru₂P, respectively. The rate constants for THFA (k_3) were 0.0185 h⁻¹ and 0.1752 h⁻¹ for RuP and Ru₂P, respectively, where no THFA was observed with MoP. From these measurements, Ru₂P displayed the highest k_3 value, which suggested high preference for THFA production. High selectivities to THFA from FOL hydrogenation have also been observed in the literature with Ru/TiO₂ along with other noble metal catalysts (Pd, Rh) and Ni boride catalysts.⁶³⁻⁶⁴ It has been noted that phosphides and borides share a similar metal-metalloid interaction (M-B and M-P) as well as B-B and P-P interactions.⁶⁵ It is plausible that the formation of THFA observed in both phosphides and borides is due to the existence of similar sites (i.e., M^{δ+} or P^{δ-}).¹⁵

The binding energy shifts of the monometallic Ru and Mo phosphides were measured with XPS to provide the relative oxidation of the materials (Table A.6). The Mo 3d_{5/2} binding energy shift was determined as 228.2 eV and 227.5 eV for MoP and Mo₃P, which were more oxidized when compared to Mo⁰ (i.e. 226.7 eV). Conversely, the P 2p_{3/2} binding energy shift was found to be 129.5 eV and 129.1 eV for MoP and Mo₃P, respectively. These values were in the range of negatively charged P (i.e. 130.0 – 130.9 eV).⁶⁶ A similar observation was also observed with the monometallic Ru phosphides. The binding energy shift of Ru 3p_{3/2} in Ru₂P (462.0 eV) is higher than RuP (461.8 eV). Both of these binding energies showed slightly oxidized Ru atoms since the binding energy shift of Ru 3p_{3/2} in Ru/Al₂O₃ was measured to be 461.6 eV. Similarly, the P atom in Ru₂P is more anionic than in RuP.

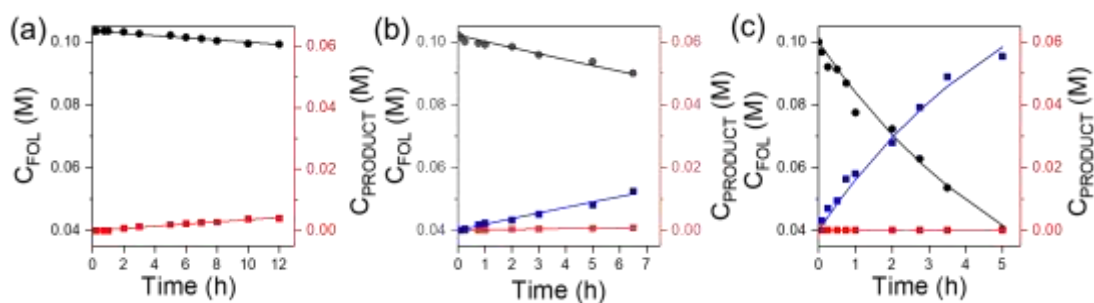


Figure 5.2. Concentration profiles for FOL (black filled circles), MF (red filled squares), and THFA (blue open squares) with (a) MoP, (b), RuP, and (c) Ru₂P determined experimentally (circles and squares) and fitted to the predicted reaction model (solid line).

X-ray absorption spectroscopy experiments were also performed for the various monometallic phosphides. From the XANES results in Table A.6 and Figure A.10, the Mo in MoP (20,001.25 eV) and Mo₃P (20,000.61 eV) are slightly oxidized compared to the Mo-foil (20,000.00 eV) with Mo₃P being less oxidized, which agrees with the XPS measurements. The Ru K-edge absorption energy for Ru₂P was determined to be 22,117.42 eV, which is also considered oxidized compared to the reference Ru foil (22,117.2 eV). Based on these results, the Mo and Ru are electron donors in the monometallic Ru and Mo phosphides, while P acts as an electron acceptor.

As shown in Table A.8, partitioning of charge density of surface atoms according to the Bader scheme reveals depletion of electronic charge density for Mo in MoP (+0.52 eV) and Mo₃P (+0.91 eV) as well as Ru in RuP (+0.11 eV) and Ru₂P (+0.13 eV). Meanwhile, the Bader charge of the P atoms were -0.52 eV, -0.91 eV, -0.11 eV, and -0.13 eV for MoP, Mo₃P, RuP, and Ru₂P. The Bader charge calculations were performed on the most dominant facet observed in XRD, which were the (101), (321), (211), and (211) for MoP, Mo₃P, RuP, and Ru₂P, respectively. These calculations also confirm the electron transfer in monometallic Ru and Mo phosphides, where Ru and Mo donate electrons to P. Taken together, XPS, XANES, and Bader charge calculations suggest that the Ru and Mo in monometallic phosphides possess Lewis acidic character (e.g., Ru^{δ+} and Mo^{δ+}), which can serve as the reactant adsorption site in metal phosphides.⁶⁷

5.3.2 Catalytic evaluation of bimetallic Ru_{1.0}Mo_{1.0}P

Our previous studies have provided evidence of catalytic enhancements with bimetallic phosphides in comparison to their monometallic counterparts.⁶⁸ Due to the high selectivity of MoP to FOL and the higher activity of RuP, we first synthesized a bimetallic Ru_{1.0}Mo_{1.0}P catalyst (Table 5.1). The k_1 , k_2 , and k_3 values for Ru_{1.0}Mo_{1.0}P were determined similarly to the methods described in the previous section at 100°C and 4.2 MPa H₂. The measured k_1 for Ru_{1.0}Mo_{1.0}P was 0.176 h⁻¹, which was >6 times higher than the monometallic MoP, RuP, and Ru₂P. This result showcased the reaction rate improvement due to inherent bimetallic effects associated with the Ru_{1.0}Mo_{1.0}P catalyst. The k_2 and k_3 values of Ru_{1.0}Mo_{1.0}P were 0.0050 h⁻¹ and 0.0039 h⁻¹, respectively. Although Ru_{1.0}Mo_{1.0}P produced both MF and THFA, the production rates were low.

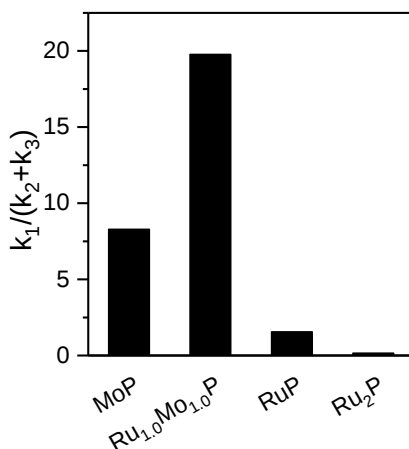


Figure 5.3. The ratio of $k_1/(k_2+k_3)$ for MoP, Ru_{1.0}Mo_{1.0}P, RuP, and Ru₂P.

The highest FOL selectivity was observed with $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ followed by $\text{MoP} > \text{RuP} > \text{Ru}_2\text{P}$, respectively. It was evident that the addition of P weakened the hydrogenation ability of Ru in the various Ru-based phosphides. Similar observations were seen in a P-doped Ru(0001) surface where the apparent charge transfer between Ru and P atoms reduced the electron back donation from Ru to the reactant.¹⁹ Moreover, the addition of Mo shifted the hydrogenation preference from aromatics to the reduction of the carbonyl in FAL. Pairing noble metals with an oxophilic metal has been reported to create bifunctional materials capable of deoxygenating biomass-derived compounds.⁶⁹ The noble metal provides a H_2 splitting site while the oxophilic metal binds the O in the reactant.⁶⁹ Similarly, it is possible that bimetallic $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ was more active compared to its monometallic counterparts due to its multifunctional behavior.

A series of experiments from ambient temperature to 150°C were performed at 4.2 MPa H_2 with $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ to study the effects of temperature on the product selectivity (Figure 5.4). The catalyst was active as low as 20°C with 4% furfural conversion observed after 15 hr (not shown). Figure 5.4 depicts the selectivity and conversion variation for $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ between 75°C – 125°C . At 75°C and 100°C , FOL is the dominant product with >99% selectivity. As the conversion increased to 60%, the selectivity at 100°C dropped to 97% due to the further reaction of

FOL on the catalyst surface to produce MF. At 125°C the selectivity to FOL dropped from 90% at low conversion to 84% at 75% conversion. The decrease in selectivity with the increase in reaction temperature is related to the effective activation barriers for each of the reactions. However, these barriers were not extracted from additional experiments because the yields of MF were not sufficient enough to provide justification for using higher temperatures to control the reaction selectivities. However, the effective activation barrier ($E_{A,1}$) was obtained during the temperature sweep experiments for the initial reduction of FAL. The activation barrier was ~51 kJ/mol, which was similar to those reported for the commercial Cu-chromite (46 kJ/mol) and Cu/SiO₂ (50 kJ/mol).^{5, 55}

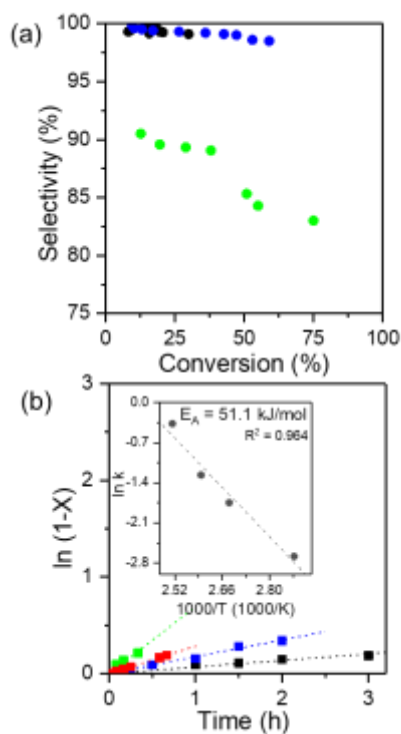


Figure 5.4. (a) FOL selectivity vs. conversion with Ru_{1.0}Mo_{1.0}P at 75°C (blue), 100°C (black), 125°C (green), and (b) linearized rate data plotted vs. time for Ru_{1.0}Mo_{1.0}P at 75°C (black – R² = 0.950), 100°C (blue – R² = 0.981), 112°C (red – R² = 0.910), 125°C (green – R² = 0.911) with an Arrhenius plot for Ru_{1.0}Mo_{1.0}P (inset).

5.3.3 Compositional variation of bimetallic Ru_xMo_{2-x}P catalysts

The kinetic studies provided evidence for catalytic enhancements with bimetallic Ru_{1.0}Mo_{1.0}P. Therefore, the composition of Ru, Mo, and P was varied in the solid solution to determine if the bimetallic effect could be further enhanced and to determine the potential causes for the observations. Moreover, the change in material composition influences the electronic properties of the bimetallic phosphides as shown for Fe_xMo_{2-x}P (0.8 < x

<1.5), where the catalytic selectivity and activity for phenol hydrodeoxygenation were both influenced by the bulk and surface compositions.⁷⁰ Therefore, in an effort to control the product selectivity, the effect of material composition in $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ was explored.

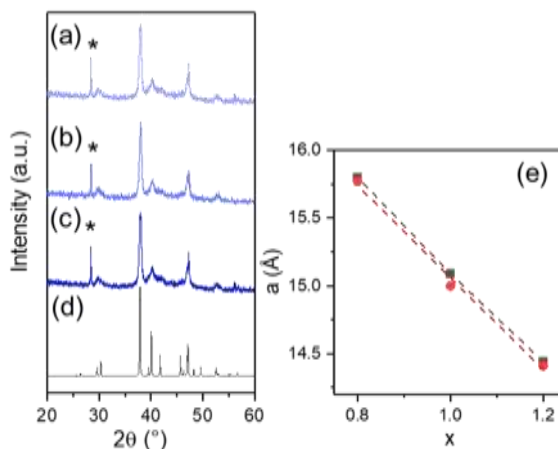


Figure 5.5. XRD patterns of $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ for (a) $x = 0.8$ (b) $x = 1.0$ (c) $x = 1.2$ and (d) $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ reference pattern (PDF 04-015-7732). (e) The lattice parameters calculated experimentally (black) and computationally (red).

Three compositions of $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ were synthesized ($x = 0.8, 1.0$, and 1.2) with all of the resulting solid solutions maintaining an orthorhombic lattice. The ratio was verified using both ICP-OES and XPS (Table A.4). The XRD patterns of $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ are presented in Figure 5.5. A Si (111) standard was added to each of the samples prior to the XRD measurement to eliminate peak shifts from the instrument. The Si (111) is marked with an asterisk (*) in Figure 5.5 and was shifted to $28.44^\circ 2\theta$. Rietveld refinement was used to calculate the lattice parameter, a , and they were compared to

the optimized, calculated lattice parameter. Figure 5.5e represents similarities between the experimental lattice parameter (black) and computationally calculated lattice parameter (red), which are within 1% error. The *b* and *c* cell dimensions are reported in Table A.3, which are also in strong agreement.

From FAL hydrogenation experiments, the k_1 values were 0.078 h^{-1} , 0.176 h^{-1} , and 0.258 h^{-1} for $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ with $x = 0.8, 1.0$, and 1.2 , respectively (Figure 5.6a). The catalytic performance of commercial $\text{Ru}/\text{Al}_2\text{O}_3$ was also analyzed to provide a comparison between a supported metal catalyst with the unsupported metal phosphides. The measured reaction rate constant for $\text{Ru}/\text{Al}_2\text{O}_3$ was 0.074 h^{-1} , which was 2-3 times higher than the monometallic phosphides, but it was about two times lower than bimetallic $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$. The FOL selectivity was not quantified due to the presence of many side products including 2-(isopropoxy)methyl furan as a result of the interaction with the solvent (isopropanol). This product was previously observed using a Ru/C catalyst for FAL hydrogenation, and it could be an intermediate to FOL production through the Meerwein-Ponndorf-Verley mechanism.⁶⁰⁻⁶¹

In addition to k_1 , both k_2 and k_3 were also determined by using the same method as described previously (Figure 5.6a). As depicted in Scheme 1, the parallel reaction pathway of FOL hydrogenation can yield both MF and THFA. However, THFA was not observed with the Mo-rich (x

= 0.8) catalyst. Figure 5.7a-c shows the concentration profiles for the reactant and product species observed using $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ where $x = 0.8, 1.0,$ and 1.2 , respectively for both the measured data (circles and squares) and predicted reaction model using k -values obtained from Equations 5-7 (lines). The model provided an excellent fit to the experimental data in the time and concentration range collected. It is important to note that the FOL hydrogenation step is significantly slower with all of the catalysts compared to the first FAL hydrogenation step.

The FOL production rate constant in $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ was examined based on the ratio between k_1 and $(k_2 + k_3)$. The ratio is plotted in Figure 5.6b with respect to x in $\text{Ru}_x\text{Mo}_{2-x}\text{P}$. Although $\text{Ru}_{1.2}\text{Mo}_{0.8}\text{P}$ has the highest k_1 value, its k_2 and k_3 were higher compared to the other bimetallic phosphides. The ratio between k_1 and $k_2 + k_3$ is the highest for $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ followed by $\text{Ru}_{1.2}\text{Mo}_{0.8}\text{P}$ and $\text{Ru}_{0.8}\text{Mo}_{1.2}\text{P}$. It is possible that the high FOL selectivity is related to the metal-metal dispersion on the metal surface, which could explain why $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ showed the highest FOL selectivity.⁹⁻¹⁰

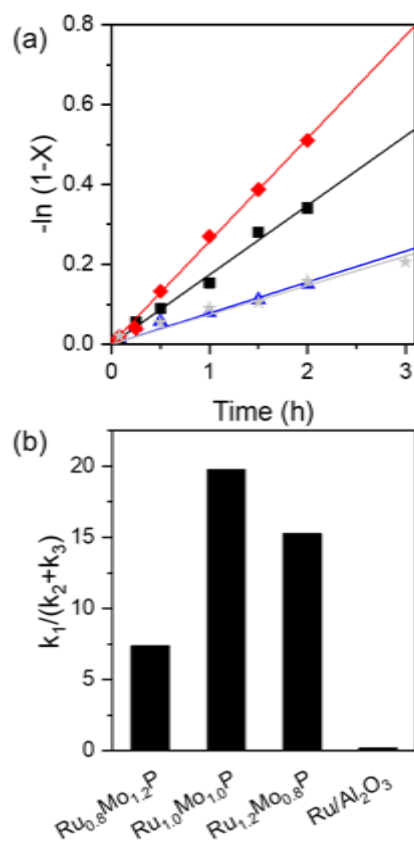


Figure 5.6. (a) Psuedo-1st order dependency of FAL with $Ru_xMo_{2-x}P$ where $x = 0.8$ (blue – $R^2 = 0.964$) and $x = 1.0$ (black – $R^2 = 0.981$), $x = 1.2$ (red – $R^2 = 0.985$), and 5% Ru/Al_2O_3 (grey – $R^2 = 0.935$) and (b) the ratio of $k_1/(k_2+k_3)$ for bimetallic $Ru_xMo_{2-x}P$ and Ru/Al_2O_3 .

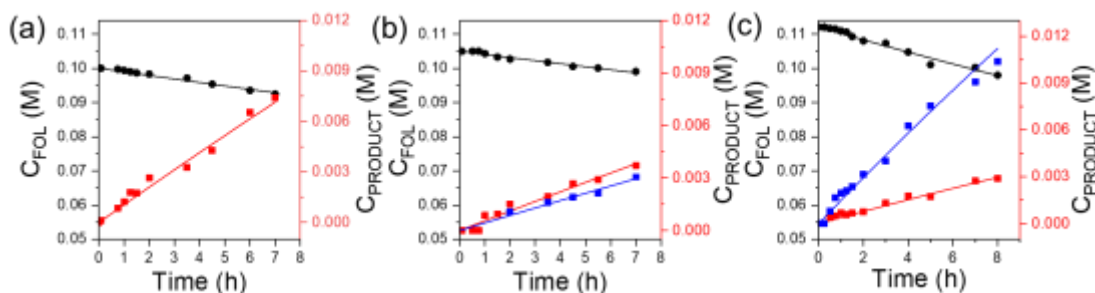


Figure 5.7. The concentration profiles of FOL (black), MF (red) and THFA (blue) obtained experimentally (circles and squares) and through model fits (straight line) for $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ where (a) $x = 0.8$, (b) $x = 1.0$, (c) $x = 1.2$

5.3.4 Theoretical and experimental surface and adsorption studies of bimetallic $\text{Ru}_x\text{Mo}_{2-x}\text{P}$

XPS was used to probe the surface oxidation on the bimetallic metal phosphides (Table 5.2). The peak deconvolution was conducted according to the methods described in the experimental section and plotted in Figure A.9. In the bimetallic RuMo phosphides, the Ru $3p_{3/2}$ was slightly negative when compared to Ru^0 at 416.6 eV. Meanwhile, the Mo was slightly positive in comparison with Mo^0 (226.8 eV). The binding energies of the phosphorus atoms were lower than P^0 (130.9 eV), suggesting anionic surface P species.⁶⁶ The XANES K-edge absorption energy of Ru and Mo are 22,116.96 eV and 20,0001.29 eV, respectively, suggesting an anionic Ru and oxidized Mo in $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ similar to the XPS result. The anionic nature of Ru is in contrast with a previous report where the Ru in $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ was reported positive.⁶⁷ This is due to the difference in

reference point used in the data analysis, which was verified herein by using a Ru/Al₂O₃ reference rather than literature values. Overall, these observation agreed with literature reports on phosphides where charge sharing is observed in metal phosphides evident by a slightly positive species (Mo) complemented by partially negative species (Ru, P).^{23, 29, 71-73} However, as shown in Table 5.2, the binding energy differences for the various bimetallic compositions were too small to draw strong correlations between these materials. The same observation was reported in (Ni_{1-x}M')₂P (*M* = Cr, Fe, Co) where the binding energy shift is around 0.1 eV resolution for different Ni to M' ratio.⁷¹

Computational calculations were performed to determine the surface and bulk charges in the different Ru_xMo_{2-x}P catalysts on the (112) surface. For comparison, additional calculations were performed on the Ru_{1.0}Mo_{1.0}P (210) facet, which resulted in nearly identical Bader charges for Ru, Mo, and P (Table A.7). The adsorption energies of furfural on the Ru_{1.0}Mo_{1.0}P (112) and (210) facets were calculated to be -3.06 eV and -3.08 eV, respectively. These small differences would not lead to significantly different adsorption results. Therefore, the (112) facet was chosen as a representative facet for the adsorption calculations. Average partial atomic charges calculated using Bader analysis on these three catalytic surfaces are presented in Table A.7. The Lewis acidic nature of Ru_{1.0}Mo_{1.0}P has been probed by pyridine adsorption using diffuse reflectance infrared

Fourier transform spectroscopy (DRIFTS) to show evidence of the presence of Lewis acid and no strong evidence of Brønsted acidity.²⁴ Since Mo is the most electron deficient atom, Mo^{δ+} is the dominant Lewis acid site in Ru_xMo_{2-x}P. Interestingly, the Mo atom in Ru_{1.0}Mo_{1.0}P contains the highest positive charge in the bulk and on the surface.

The Bader charge for Ru in Ru_xMo_{2-x}P was negative to show that Ru is an electron acceptor in the Ru_{1.0}Mo_{1.0}P system (Table 5.2). Although the negative charge on Ru is non-intuitive, Mulliken charge analysis in Ru_{1.0}Mo_{1.0}P also showed that Ru can act as an electron acceptor.⁷⁴ Moreover, similar effects have been reported in bimetallic Ce-doped Co phosphides, where the Co becomes negative with Ce addition.⁷⁵ However, caution should be applied when comparing Bader charge calculations and experimentally obtained results due to the complicated nature of the metallic states and the simplified system applied with the Bader charge calculation.⁷⁶⁻⁷⁷ Nevertheless, the XPS, XANES, and Bader charge analysis indicated the same electron flow from Mo to Ru and P in bimetallic Ru_{1.0}Mo_{1.0}P.

Computationally, the average positive partial charge on the Mo atoms on the catalytic surfaces followed the order: Ru_{1.2}Mo_{0.8}P (+0.54 |e|) < Ru_{0.8}Mo_{1.2}P (+0.62 |e|) < Ru_{1.0}Mo_{1.0}P (+0.70 |e|), which suggested more average positive charge in Ru_{1.0}Mo_{1.0}P. This greater charge transfer (from

Mo to Ru and P atoms) could potentially lead to stronger binding with the electron rich carbonyl O in furfural with $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$. It is important to note that the surface charge could also be correlated with the selectivity, where more positive charge on Mo leads to higher FOL selectivity.

Other reports have shown that the furfural orientation plays an important role in the reaction selectivity.^{55, 78-82} The two binding modes that have been suggested to be most favorable in furfural adsorption are $\eta^1(\text{O})$ and $\eta^2(\text{C-O})$ (Figure A.11).^{55, 80} The $\eta^1(\text{O})$ surface configuration was suggested from an FTIR experiment using a Cu catalyst where the O of the carbonyl interacts with the surface to preferably produce FOL.⁵⁵ Meanwhile, the $\eta^2(\text{C-O})$ mode was suggested in group VIII catalysts through DFT calculations where both of the C and O from the C=O carbonyl of FAL interact with the surface leading to the formation of MF and furan.⁸⁰ The $\eta^1(\text{O})$ surface interaction was studied experimentally with DRIFTS and theoretically with DFT calculations in this work. Meanwhile the $\eta^2(\text{C-O})$ interaction was not observed,⁸³⁻⁸⁵ but it was observed in other work using high resolution electron energy loss (HREEL) spectroscopy.⁸⁶ The adsorption mode was of interest as a potential descriptor for the product selectivity distribution in FAL hydrogenation. Furthermore, others have reported the incorporation of Cu into Pd decreases the amount of decarbonylation product due to the shift from $\eta^2(\text{C-O})$ in Pd to $\eta^1(\text{O})$ in Pd-

Cu.⁸⁷ For the same reason, the incorporation of Mo in $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ may provide a FOL selectivity shift.

DRIFTS was therefore performed on the synthesized phosphide catalysts after adsorption of furfural vapor. The DRIFTS experiment was based on previous report that showed the existence of $\eta^1(\text{O})$ adsorption mode in IR spectroscopy.⁵⁵ The catalyst surface was saturated with a stream of N_2 that passed through a FAL bubbler at 200°C for 50 mins. The saturation point was indicated by the existence of two peaks at 1720 cm^{-1} from gas phase furfural C=O stretching vibration and 1670 cm^{-1} from C-O stretching band in the adsorbed FAL species as can be seen Figure A.12.⁵⁵

The adsorbed C-O vibration mode was observed at a lower wavenumber from the gas phase FAL due to a weakened C-O bond resulting from the C=O adsorption on the surface through a $\eta^1(\text{O})$ -type of interaction. This result indicated that the same carbonyl configuration in $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ was observed with the Cu-catalyst. Interestingly, the adsorbed C-O vibration mode can also be observed in the DRIFTS experiments for all monometallic MoP, RuP, Ru_2P as well as bimetallic $\text{Ru}_{0.8}\text{Mo}_{1.2}\text{P}$ and $\text{Ru}_{1.2}\text{Mo}_{0.8}\text{P}$ (Figure A.12) yet these catalysts have different selectivities for furfural hydrogenation. Therefore, the DRIFTS peak at $\sim 1670\text{ cm}^{-1}$ could not be correlated with the selectivity with MoP, RuP, Ru_2P , $\text{Ru}_{0.8}\text{Mo}_{1.2}\text{P}$, $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$, and $\text{Ru}_{1.2}\text{Mo}_{0.8}\text{P}$.

TABLE 5.2.
BINDING ENERGY SHIFT, SURFACE, AND BULK BADER CHARGES OF
Ru_xMo_{2-x}P ON THE (112) FACET AND BINDING ENERGY SHIFT FROM
XPS.

	Binding energy (eV)			Surface energy (eV)			Bulk energy (eV)		
	Ru	Mo	P	Ru	Mo	P	Ru	Mo	P
Ru _{0.8} Mo _{1.2} P	461.5	228.2	129.0	-0.21	+0.62	-0.41	-0.15	+0.20	-0.19
Ru _{1.0} Mo _{1.0} P	461.5	228.2	129.1	-0.23	+0.70	-0.46	-0.18	+0.70	-0.18
Ru _{1.2} Mo _{0.8} P	461.4	228.1	129.2	-0.29	+0.54	-0.25	-0.13	+0.67	-0.11

DFT calculations in the gas phase were performed to benchmark the adsorption energies of FAL on the bimetallic Ru_xMo_{2-x}P to the literature. The adsorption energy of *trans*-furfural (Figure 5.8a-c) and *cis*-furfural (Figure 5.8d-f) on Ru_{0.8}Mo_{1.2}P, Ru_{1.0}Mo_{1.0}P, and Ru_{1.2}Mo_{0.8}P were evaluated. The adsorption energies were found to be ~0.07 – 0.31 eV higher for *trans*-furfural, which suggested more favorable adsorption of *trans*-furfural. The result was in an agreement with the previous theoretical studies.⁸⁸⁻⁸⁹ The center of mass (COM) was calculated for FAL and Ru_xMo_{2-x}P (Table A.9). Based on the DFT calculation, the COM distance to the surface was calculated to be 1.73 Å, 1.68 Å, and 3.51 Å for Ru_{0.8}Mo_{1.2}P, Ru_{1.0}Mo_{1.0}P, and Ru_{1.2}Mo_{0.8}P respectively. The COM was found to be the shortest in Ru_{1.0}Mo_{1.0}P. Additionally, the Mo-O distance was calculated to be the shortest on Ru_{1.0}Mo_{1.0}P (1.68 Å), Ru_{0.8}Mo_{1.2}P

(1.80 Å), and Ru_{1.2}Mo_{0.8}P (1.87 Å), respectively, which suggested that the carbonyl O would preferably interact with the more oxophilic metal (i.e. Mo). The calculation also suggested that Mo-O interaction might be crucial in selective FAL hydrogenation to FOL as the shortest Mo-O distance was found in the most selective catalyst, Ru_{1.0}Mo_{1.0}P.

The adsorption energies for *trans*-furfural were calculated as -2.52 eV, -3.06 eV, and -2.12 eV for Ru_{0.8}Mo_{1.2}P, Ru_{1.0}Mo_{1.0}P, and Ru_{1.2}Mo_{0.8}P, respectively, and their corresponding binding orientation was represented in Figure 5.8a-c. The adsorption energy results were in a similar range with the reported furfural adsorption on supported and unsupported metal catalysts.^{9, 79, 88-92} For example, the reported FAL adsorption energy on Pt(111), Pt(211), and Pt₅₅ surface were -1.36 eV, -1.95 eV, and -2.52 eV respectively.⁷⁹ Similarly, the adsorption energy on Pd(111) was found to be -1.83.⁸⁹ Interestingly, the reported FAL adsorption energy on Cu(111) was in the range of -0.05 to -0.17 eV, which was significantly lower.⁵⁵ This might be due to less interaction between FAL and the surface since the tilted configuration was favored in Cu(111). It can be seen from Figure 5.8a-c, the FAL molecule interacted with the catalyst surface not only through the carbonyl O but also through the carbonyl C and furan ring. This type of interaction has been suggested to follow the FAL $\eta^2(\text{C-O})$ adsorption mode to produce MF.⁸⁰ Since the calculation was done in the gas phase, the DFT result was in agreement with the experimental result at higher temperature

where other hydrogenation products were observed. Additionally, high MF selectivity in the gas phase reactions have been observed in other works using MoP and Ni₂P.^{22, 93}

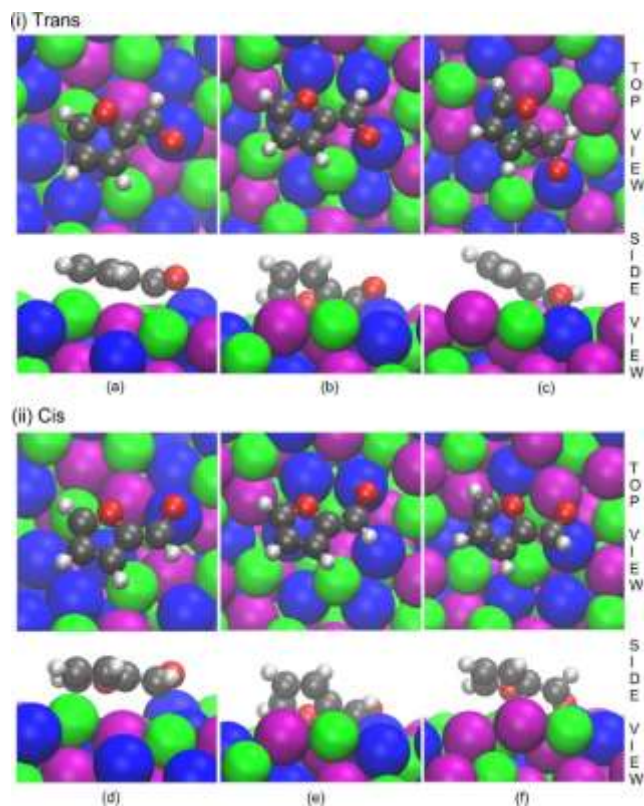


Figure 5.8. Adsorption of (i) trans- and (ii) cis-furfural on the (112) facets for (a) Ru_{0.8}Mo_{1.2}P, (b) Ru_{1.0}Mo_{1.0}P, and (c) Ru_{1.2}Mo_{0.8}P catalyst in the horizontal mode. The atom colors are purple for Ru, blue for Mo, green for P, grey for C, silver for H, and red for O.

However, the DFT calculation could not represent the experimental result since the calculation was done in the gas phase while the reaction was performed in a condensed phase. The discrepancy could be due to the absence of other surface species in the DFT calculation such as

solvents. Multiple studies have suggested solvents influenced the FAL conversion and FOL selectivity.^{16, 94} Therefore, toluene and hexanes were used as solvents for FAL hydrogenation at the same reaction condition of 100°C and 4.2 MPa with 0.10 M starting concentration. According to the reaction results (Figure 5.9), the conversion decreased significantly in toluene and hexanes, which was consistent with previous observations. The selectivity towards FOL also decreased significantly from >99% with isopropanol to 88% in toluene and 65% in hexanes. The result showed that solvent selection can greatly influence the selectivity to FOL. As noted earlier, background experiments using isopropanol as a H₂-donor resulted in negligible conversion. The solvent effect on the surface configuration and the elucidation of reaction mechanisms are ongoing projects in our research groups.

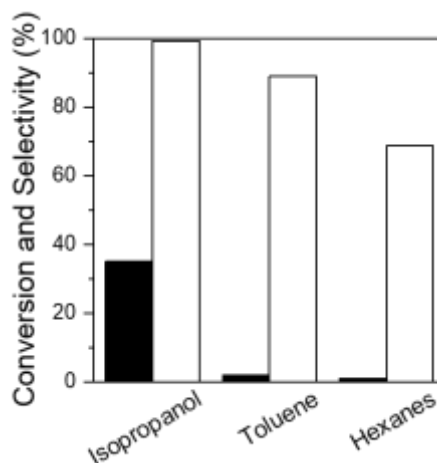


Figure 5.9. The effect of solvents towards FAL conversion (filled) and FOL selectivity (empty). The data were recorded after 3 h.

5.3.5 Catalyst recyclability

Catalyst stability is one of the major problems with copper chromite, as it was reported to decrease by 40% in 4 h.⁸ The deactivation has been attributed to carbonaceous formations, leaching, and sintering.^{7-8, 95-98} Therefore, a stability study was performed with Ru_{1.0}Mo_{1.0}P through recycling experiments.

The stability of Ru_{1.0}Mo_{1.0}P was tested with three recycling experiments. Each of the experiments was performed using 25.0 mg of catalyst for 6 hr at 100°C and 4.2 MPa. The reaction rate constant, k_1 , was determined from each of the runs as well as the FAL conversion and FOL selectivity after 6 hrs. The results are presented in Figure 5.10. Based on the recycling experiments, the conversion at 6 h decreased slightly from 69% to 65% on the second cycle and finally to 61% on the final cycle. The

reaction rate constant also decreased from 0.176 h^{-1} on the first cycle to 0.171 h^{-1} and 0.165 h^{-1} for the second and third cycle, respectively. Meanwhile the selectivity towards FOL remained high at $>97\%$ for all cycles. The deactivation seen from each cycle could be due to surface oxidation during a drying step between the cycles. To overcome this issue, re-reduction at 650°C for 2 h under 160 mL/min of H_2 was conducted on the materials recovered from the third cycle. The re-reduced material was then tested at the same reaction condition by loading the same catalyst weight. In the fourth cycle, the conversion was recovered back to 71% with a selectivity of 96%.

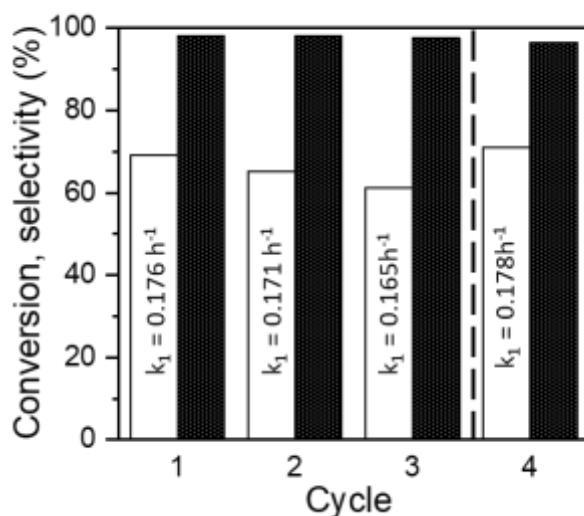


Figure 5.10. Conversion (empty) and FOL selectivity (shaded) of $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ for FAL hydrogenation at 4.2 MPa and 100°C in recycling experiment. The dotted line signifies re-reduction.

5.4 Conclusions

The hydrogenation of FAL was successfully demonstrated over a series of monometallic phosphides (MoP, RuP, Ru₂P) and bimetallic phosphides (Ru_xMo_{2-x}P for $x = 0.8, 1.0$, and 1.2). Bimetallic Ru_{1.0}Mo_{1.0}P and monometallic MoP exhibited high selectivity (99%) towards FOL production in FAL hydrogenation with minimal production of MF. The catalytic results also showed that a bimetallic effect was observed through an increase in the reaction rate of furfural with bimetallic Ru_xMo_{2-x}P compared to its monometallic analogues. Kinetic evaluation determined an activation energy (E_A) of 51.1 kJ/mol for Ru_{1.0}Mo_{1.0}P, which was comparable to Cu-based catalysts reported in the literature. The ratio between k_1/k_2+k_3 was found to be the highest with Ru_{1.0}Mo_{1.0}P > Ru_{1.2}Mo_{0.8}P > MoP > Ru_{0.8}Mo_{1.2}P > RuP > Ru₂P, which suggested that the production of FOL per reaction rate was more favored with Ru_{1.0}Mo_{1.0}P. DFT calculations in the gas phase showed the most favorable adsorption on Ru_{1.0}Mo_{1.0}P > Ru_{0.8}Mo_{1.2}P > Ru_{1.2}Mo_{0.8}P which was consistent with the FOL selectivity trend. Additionally, the use of isopropanol was found to positively influence the selectivity to FOL, while non-polar solvents (toluene and hexanes) decreased the conversion and selectivity. Lastly, we have shown that Ru_{1.0}Mo_{1.0}P can be recovered to its original rate through re-reduction. Overall, this study provides strong support for the use of bimetallic

phosphides for furfural hydrogenation to furfuryl alcohol as well as other selective hydrogenation reactions.

5.5 References

1. Li, X. D.; Jia, P.; Wang, T. F., Furfural: A promising platform compound for sustainable production of C-4 and C-5 chemicals. *ACS Catal.* **2016**, *6* (11), 7621-7640.
2. Serrano-Ruiz, J. C.; Luque, R.; Sepulveda-Escribano, A., Transformations of biomass-derived platform molecules: from high added-value chemicals to fuels via aqueous-phase processing. *Chem. Soc. Rev.* **2011**, *40* (11), 5266-5281.
3. Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sadaba, I.; Granados, M. L., Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels. *Energ Environ Sci* **2016**, *9* (4), 1144-1189.
4. Bauer, K.; Panten, J.; Surburg, H., *Common fragrance and flavor materials : preparation, properties and uses*. Weinheim : Wiley-VCH: 2016.
5. Rao, R.; Dandekar, A.; Baker, R. T. K.; Vannice, M. A., Properties of copper chromite catalysts in hydrogenation reactions. *J. Catal.* **1997**, *171* (2), 406-419.
6. Connor, R.; Folkers, K.; Adkins, H., The preparation of copper-chromium oxide catalysts for hydrogenation. *J. Am. Chem. Soc.* **1931**, *53* (2), 2012-2012.
7. Zhang, H. B.; Lei, Y.; Kropf, A. J.; Zhang, G. H.; Elam, J. W.; Miller, J. T.; Sollberger, F.; Ribeiro, F.; Akatay, M. C.; Stach, E. A.; Dumesic, J. A.; Marshall, C. L., Enhancing the stability of copper chromite catalysts for the selective hydrogenation of furfural using ALD overcoating. *J. Catal.* **2014**, *317*, 284-292.
8. Liu, D. X.; Zemlyanov, D.; Wu, T. P.; Lobo-Lapidus, R. J.; Dumesic, J. A.; Miller, J. T.; Marshall, C. L., Deactivation mechanistic studies of copper chromite catalyst for selective hydrogenation of 2-furfuraldehyde. *J. Catal.* **2013**, *299*, 336-345.
9. Seemala, B.; Cai, C. M.; Kumar, R.; Wyman, C. E.; Christopher, P., Effects of Cu-Ni bimetallic catalyst composition and support on activity,

selectivity, and stability for furfural conversion to 2-methylfuran. *ACS Sustain. Chem. Eng.* **2018**, 6 (2), 2152-2161.

10. Sheng, H.; Lobo, R. F., Iron-promotion of silica-supported copper catalysts for furfural hydrodeoxygenation. *ChemCatChem* **2016**, 8 (21), 3402-3408.
11. Srivastava, S.; Jadeja, G. C.; Parikh, J., Copper-cobalt catalyzed liquid phase hydrogenation of furfural to 2-methylfuran: An optimization, kinetics and reaction mechanism study. *Chem. Eng. Res. Des.* **2018**, 132, 313-324.
12. Srivastava, S.; Solanki, N.; Mohanty, P.; Shah, K. A.; Parikh, J. K.; Dalai, A. K., Optimization and kinetic studies on hydrogenation of furfural to furfuryl alcohol over SBA-15 supported bimetallic copper-cobalt catalyst. *Catal. Lett.* **2015**, 145 (3), 816-823.
13. Jimenez-Gomez, C. P.; Cecilia, J. A.; Duran-Martin, D.; Moreno-Tost, R.; Santamaria-Gonzalez, J.; Merida-Robles, J.; Mariscal, R.; Maireles-Torres, P., Gas-phase hydrogenation of furfural to furfuryl alcohol over Cu/ZnO catalysts. *J. Catal.* **2016**, 336, 107-115.
14. Yan, K.; Chen, A. C., Selective hydrogenation of furfural and levulinic acid to biofuels on the ecofriendly Cu-Fe catalyst. *Fuel* **2014**, 115, 101-108.
15. Merat, N.; Godawa, C.; Gaset, A., High selective production of tetrahydrofurfuryl alcohol - catalytic hydrogenation of furfural and furfuryl alcohol. *J. Chem. Technol. Biotechnol.* **1990**, 48 (2), 145-159.
16. Merlo, A. B.; Vetere, V.; Ruggera, J. F.; Casella, M. L., Bimetallic PtSn catalyst for the selective hydrogenation of furfural to furfuryl alcohol in liquid-phase. *Catal. Commun.* **2009**, 10 (13), 1665-1669.
17. Musci, J. J.; Merlo, A. B.; Casella, M. L., Aqueous phase hydrogenation of furfural using carbon-supported Ru and RuSn catalysts. *Catal. Today.* **2017**, 296, 43-50.
18. O'Driscoll, A.; Curtin, T.; Hernandez, W. Y.; Van Der Voort, P.; Leahy, J. J., Hydrogenation of furfural with a Pt-Sn catalyst: the suitability to sustainable industrial application. *Org Process Res Dev* **2016**, 20 (11), 1917-1929.
19. Sampath, A.; Chang, S. A.; Flaherty, D. W., Catalytic hydrogen transfer and decarbonylation of aromatic aldehydes on Ru and Ru phosphide model catalysts. *The Journal of Physical Chemistry C* **2018**, 122 (41), 23600-23609.

20. Habas, S. E.; Baddour, F. G.; Ruddy, D. A.; Nash, C. P.; Wang, J.; Pan, M.; Hensley, J. E.; Schaidle, J. A., A Facile Molecular Precursor Route to Metal Phosphide Nanoparticles and Their Evaluation as Hydrodeoxygenation Catalysts. *Chem. Mater.* **2015**, *27* (22), 7580-7592.
21. Bowker, R. H.; Smith, M. C.; Pease, M. L.; Slenkamp, K. M.; Kovarik, L.; Bussell, M. E., Synthesis and hydrodeoxygenation properties of ruthenium phosphide catalysts. *ACS Catal.* **2011**, *1* (8), 917-922.
22. Jiménez-Gómez, C. P.; Cecilia, J. A.; Moreno-Tost, R.; Maireles-Torres, P., Nickel Phosphide/Silica Catalysts for the Gas-Phase Hydrogenation of Furfural to High-Added-Value Chemicals. *Chemcatchem* **2017**, *9* (14), 2881-2889.
23. Bonita, Y.; Hicks, J. C., Periodic trends from metal substitution in bimetallic Mo-based phosphides for hydrodeoxygenation and hydrogenation reactions. *J. Phys. Chem. C* **2018**, *122* (25), 13322-13332.
24. Bonita, Y.; O'Connell, T. P.; Miller, H. E.; Hicks, J. C., Revealing the hydrogenation performance of RuMo phosphide for chemoselective reduction of functionalized aromatic hydrocarbons. *Ind. Eng. Chem. Res.* **2019**, *58* (9), 3650-3658.
25. Bonita, Y.; Jain, V.; Geng, F.; O'Connell, T. P.; Wilson, W. N.; Rai, N.; Hicks, J. C., Direct synthesis of furfuryl alcohol from furfural: catalytic performance of monometallic and bimetallic Mo and Ru phosphides. *Catal. Sci. Technol.* **2019**, *9* (14), 3656-3668.
26. Corro, G.; Gomez, R., Carbon-monoxide adsorption and hydrogen-oxygen titration on Ru-Al₂O₃. *React. Kinet. Catal. L.* **1979**, *12* (2), 145-150.
27. Doniach, S.; Sunjic, M., Many-electron singularity in x-ray photoemission and x-ray line spectra from metals. *J. Phys. C* **1970**, *3* (2), 285-&.
28. Morgan, D. J., Resolving ruthenium: XPS studies of common ruthenium materials. *Surf. Interface Anal.* **2015**, *47* (11), 1072-1079.
29. Blanchard, P. E. R.; Grosvenor, A. P.; Cavell, R. G.; Mar, A., X-ray photoelectron and absorption spectroscopy of metal-rich phosphides M₂P and M₃P (M = Cr-Ni). *Chem. Mater.* **2008**, *20* (22), 7081-7088.
30. Becke, A. D., Perspective: Fifty years of density-functional theory in chemical physics. *J. Chem. Phys.* **2014**, *140* (18).
31. Parr, R. G., Density functional theory of atoms and molecules. *Horizons of Quantum Chemistry* **1980**, 5-15.

32. Kresse, G.; Hafner, J., Abinitio molecular-dynamics for liquid-metals. *Phys. Rev. B* **1993**, 47 (1), 558-561.
33. Kresse, G.; Hafner, J., Ab-Initio molecular-dynamics simulation of the liquid-metal amorphous-semiconductor transition in germanium. *Phys. Rev. B* **1994**, 49 (20), 14251-14269.
34. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, 54 (16), 11169-11186.
35. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.* **1996**, 6 (1), 15-50.
36. Klimeš, J.; Bowler, D. R.; Michaelides, A., Van der Waals density functionals applied to solids. *Phys. Rev. B* **2011**, 83 (19).
37. Klimeš, J.; Bowler, D. R.; Michaelides, A., Chemical accuracy for the van der Waals density functional. *J. Phys. Condens. Matter* **2009**, 22 (2), 022201.
38. Blöchl, P. E., Projector augmented-wave method. *Phys. Rev. B* **1994**, 50 (24), 17953-17979.
39. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, 59 (3), 1758-1775.
40. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab-Initio calculation of vibrational absorption and circular-dichroism spectra using density-functional force-fields. *J. Phys. Chem.* **1994**, 98 (45), 11623-11627.
41. Methfessel, M.; Paxton, A. T., High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* **1989**, 40 (6), 3616-3621.
42. Genova, A.; Pavanello, M., Exploiting the locality of periodic subsystem density-functional theory: efficient sampling of the Brillouin zone. *J. Phys. Condens. Matter* **2015**, 27 (49).
43. Henkelman, G.; Arnaldsson, A.; Jónsson, H., A fast and robust algorithm for Bader decomposition of charge density. *Comp. Mater. Sci.* **2006**, 36 (3), 354-360.
44. Yu, M.; Trinkle, D. R., Accurate and efficient algorithm for Bader charge integration. *J. Chem. Phys.* **2011**, 134 (6), 064111.

45. Tang, W.; Sanville, E.; Henkelman, G., A grid-based Bader analysis algorithm without lattice bias. *J. Phys. Condens. Matter* **2009**, *21* (8), 084204.
46. Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G., Improved grid-based algorithm for Bader charge allocation. *J. Comput. Chem.* **2007**, *28* (5), 899-908.
47. Stinner, C.; Prins, R.; Weber, T., Formation, structure, and HDN activity of unsupported molybdenum phosphide. *J. Catal.* **2000**, *191* (2), 438-444.
48. Whiffen, V. M. L.; Smith, K. J., Hydrodeoxygenation of 4-methylphenol over unsupported MoP, MoS₂, and MoO_x catalysts. *Energ. Fuel* **2010**, *24*, 4728-4737.
49. Wang, R.; Smith, K. J., Preparation of Unsupported NiMoP Catalysts for 4,6-Dimethyldibenzothiophene Hydrodesulfurization. *Catal. Lett.* **2014**, *144* (9), 1594-1601.
50. Whiffen, V. M. L.; Smith, K. J.; Straus, S. K., The influence of citric acid on the synthesis and activity of high surface area MoP for the hydrodeoxygenation of 4-methylphenol. *Appl. Catal. A* **2012**, *419*, 111-125.
51. Oyama, S. T., Novel catalysts for advanced hydroprocessing: transition metal phosphides. *J. Catal.* **2003**, *216* (1-2), 343-352.
52. Sawhill, S. J.; Layman, K. A.; Van Wyk, D. R.; Engelhard, M. H.; Wang, C.; Bussell, M. E., Thiophene hydrodesulfurization over nickel phosphide catalysts: effect of the precursor composition and support. *J. Catal.* **2005**, *231* (2), 300-313.
53. Vaidya, P. D.; Mahajani, V. V., Kinetics of liquid-phase hydrogenation of furfuraldehyde to furfuryl alcohol over a Pt/C catalyst. *Ind. Eng. Chem. Res.* **2003**, *42* (17), 3881-3885.
54. Rao, R. S.; Baker, R. T. K.; Vannice, M. A., Furfural hydrogenation over carbon-supported copper. *Catal. Lett.* **1999**, *60* (1-2), 51-57.
55. Sitthisa, S.; Sooknoi, T.; Ma, Y. G.; Balbuena, P. B.; Resasco, D. E., Kinetics and mechanism of hydrogenation of furfural on Cu/SiO₂ catalysts. *J. Catal.* **2011**, *277* (1), 1-13.
56. Pang, S. H.; Medlin, J. W., Adsorption and reaction of furfural and furfuryl alcohol on Pd(111): unique reaction pathways for multifunctional reagents. *ACS Catal.* **2011**, *1* (10), 1272-1283.

57. Dean, R. B.; Dixon, W. J., Simplified Statistics for Small Numbers of Observations. *Anal. Chem.* **1951**, 23 (4), 636-638.
58. Jaatinen, S.; Tournon, J.; Karinen, R.; Uusi-Kyyny, P.; Alopaeus, V., Hydrogen solubility in furfural and 2-propanol: Experiments and modeling. *J. Chem. Thermodyn.* **2017**, 112, 1-6.
59. Xiao, P.; Sk, M. A.; Thia, L.; Ge, X. M.; Lim, R. J.; Wang, J. Y.; Lim, K. H.; Wang, X., Molybdenum phosphide as an efficient electrocatalyst for the hydrogen evolution reaction. *Energ Environ Sci* **2014**, 7 (8), 2624-2629.
60. Panagiotopoulou, P.; Vlachos, D. G., Liquid phase catalytic transfer hydrogenation of furfural over a Ru/C catalyst. *Appl. Catal. A* **2014**, 480, 17-24.
61. Koehle, M.; Lobo, R. F., Lewis acidic zeolite beta catalyst for the Meerwein-Ponndorf-Verley reduction of furfural. *Catal. Sci. Technol.* **2016**, 6 (9), 3018-3026.
62. Luo, J.; Yu, J.; Gorte, R. J.; Mahmoud, E.; Vlachos, D. G.; Smith, M. A., The effect of oxide acidity on HMF etherification. *Catal. Sci. Technol.* **2014**, 4 (9), 3074-3081.
63. Tike, M. A.; Mahajani, V. V., Kinetics of liquid-phase hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol over a Ru/TiO₂ catalyst. *Ind. Eng. Chem. Res.* **2007**, 46 (10), 3275-3282.
64. Song, Y.; Li, W.; Zhang, M.; Tao, K., Hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol on NiB/SiO₂ amorphous alloy catalyst. *Frontiers of Chemical Engineering in China* **2007**, 1 (2), 151-154.
65. Carencu, S.; Portehault, D.; Boissiere, C.; Mezailles, N.; Sanchez, C., Nanoscaled metal borides and phosphides: recent developments and perspectives. *Chem. Rev.* **2013**, 113 (10), 7981-8065.
66. Pelavin, M.; Hendrickson, D. N.; Hollander, J. M.; Jolly, W. L., Phosphorus 2p electron binding energies: correlation with extended Huckel charges. *J. Phys. Chem.* **1970**, 74 (5).
67. Jain, V.; Bonita, Y.; Brown, A.; Taconi, A.; Hicks, J. C.; Rai, N., Mechanistic insights into hydrodeoxygenation of phenol on bimetallic phosphide catalysts. *Catal. Sci. Technol.* **2018**, 8 (16), 4083-4096.
68. Rensel, D. J.; Rouvimov, S.; Gin, M. E.; Hicks, J. C., Highly selective bimetallic FeMoP catalyst for C-O bond cleavage of aryl ethers. *J. Catal.* **2013**, 305, 256-263.

69. Robinson, A. M.; Hensley, J. E.; Medlin, J. W., Bifunctional catalysts for upgrading of biomass-derived oxygenates: a review. *ACS Catal.* **2016**, 6 (8), 5026-5043.
70. Rensel, D. J.; Kim, J.; Jain, V.; Bonita, Y.; Rai, N.; Hicks, J. C., Composition-directed $\text{Fe}_x\text{Mo}_{2-x}\text{P}$ bimetallic catalysts for hydrodeoxygenation reactions. *Catal. Sci. Technol.* **2017**, 7, 1857-1867.
71. Blanchard, P. E. R.; Grosvenor, A. P.; Cavell, R. G.; Mar, A., Effects of metal substitution in transition-metal phosphides ($\text{Ni}_{1-x}\text{M}'_x$)(2)P ($\text{M}' = \text{Cr, Fe, Co}$) studied by X-ray photoelectron and absorption spectroscopy. *J. Mater. Chem.* **2009**, 19 (33), 6015-6022.
72. Grosvenor, A. P.; Cavell, R. G.; Mar, A., Next-nearest neighbour contributions to P 2p(3/2) X-ray photoelectron binding energy shifts of mixed transition-metal phosphides $\text{M}_{1-x}\text{M}'_x\text{P}$ with the MnP-type structure. *J. Solid State Chem.* **2007**, 180 (10), 2702-2712.
73. Grosvenor, A. P.; Wik, S. D.; Cavell, R. G.; Mar, A., Examination of the bonding in binary transition-metal monophosphides MP ($\text{M} = \text{Cr, Mn, Fe, Co}$) by x-ray photoelectron spectroscopy. *Inorg. Chem.* **2005**, 44 (24), 8988-8998.
74. Wong-Ng, W.; Ching, W. Y.; Xu, Y.-N.; Kaduk, J. A.; Shirotani, I.; Swartzendruber, L., Structure and electronic properties of the orthorhombic MoRuP superconductor prepared at high pressure. *Phys. Rev. B.* **2003**, 67 (14), 144523.
75. Gao, W.; Yan, M.; Cheung, H.-Y.; Xia, Z.; Zhou, X.; Qin, Y.; Wong, C.-Y.; Ho, J. C.; Chang, C.-R.; Qu, Y., Modulating electronic structure of CoP electrocatalysts towards enhanced hydrogen evolution by Ce chemical doping in both acidic and basic media. *Nano Energy* **2017**, 38, 290-296.
76. Walsh, A.; Sokol, A. A.; Buckeridge, J.; Scanlon, D. O.; Catlow, C. R. A., Electron counting in solids: oxidation states, partial charges, and ionicity. *J. Phys. Chem. Lett.* **2017**, 8 (9), 2074-2075.
77. Walsh, A.; Sokol, A. A.; Buckeridge, J.; Scanlon, D. O.; Catlow, C. R. A., Oxidation states and ionicity. *Nat. Mater.* **2018**, 17 (11), 958-964.
78. Pang, S. H.; Schoenbaum, C. A.; Schwartz, D. K.; Medlin, J. W., Directing reaction pathways by catalyst active-site selection using self- assembled monolayers. *Nat Commun* **2013**, 4.

79. Cai, Q. X.; Wang, J. G.; Wang, Y. G.; Mei, D. H., Mechanistic insights into the structure-dependent selectivity of catalytic furfural conversion on platinum catalysts. *Aiche J* **2015**, *61* (11), 3812-3824.
80. Sitthisa, S.; An, W.; Resasco, D. E., Selective conversion of furfural to methylfuran over silica-supported Ni-Fe bimetallic catalysts. *J. Catal.* **2011**, *284* (1), 90-101.
81. Sitthisa, S.; Resasco, D. E., Hydrodeoxygenation of furfural over supported metal catalysts: a comparative study of Cu, Pd and Ni. *Catal. Lett.* **2011**, *141* (6), 784-791.
82. Qian, M.-d.; Xue, J.-l.; Xia, S.-j.; Ni, Z.-m.; Jiang, J.-h.; Cao, Y.-y., Decarbonylation and hydrogenation reaction of furfural on Pd/Cu(111) surface. *J. Fuel Chem. Technol.* **2017**, *45* (1), 34-42.
83. Greenler, R. G.; Snider, D. R.; Witt, D.; Sorbello, R. S., The metal-surface selection rule for infrared-spectra of molecules adsorbed on small metal particles. *Surf. Sci.* **1982**, *118* (3), 415-428.
84. Greenler, R. G., Infrared Study of Adsorbed Molecules on Metal Surfaces by Reflection Techniques. *The Journal of Chemical Physics* **1966**, *44* (1), 310-315.
85. Pearce, H. A.; Sheppard, N., Possible importance of a “metal-surface selection rule” in the interpretation of the infrared spectra of molecules adsorbed on particulate metals; infrared spectra from ethylene chemisorbed on silica-supported metal catalysts. *Surf. Sci.* **1976**, *59* (1), 205-217.
86. Davis, J. L.; Barteau, M. A., Spectroscopic identification of alkoxide, aldehyde, and acyl intermediates in alcohol decomposition on Pd(111). *Surf. Sci.* **1990**, *235* (2-3), 235-248.
87. Sitthisa, S.; Pham, T.; Prasomsri, T.; Sooknoi, T.; Mallinson, R. G.; Resasco, D. E., Conversion of furfural and 2-methylpentanal on Pd/SiO₂ and Pd-Cu/SiO₂ catalysts. *J. Catal.* **2011**, *280* (1), 17-27.
88. Shi, Y.; Zhu, Y. L.; Yang, Y.; Li, Y. W.; Jiao, H. J., Exploring furfural catalytic conversion on Cu(111) from computation. *ACS Catal.* **2015**, *5* (7), 4020-4032.
89. Liu, B.; Cheng, L.; Curtiss, L.; Greeley, J., Effects of van der Waals density functional corrections on trends in furfural adsorption and hydrogenation on close-packed transition metal surfaces. *Surf. Sci.* **2014**, *622*, 51-59.

90. Wang, S.; Vorotnikov, V.; Sutton, J. E.; Vlachos, D. G., Bronsted-Evans-Polanyi and transition state scaling relations of furan derivatives on Pd(111) and their relation to those of small molecules. *ACS Catal.* **2014**, *4* (2), 604-612.
91. Vorotnikov, V.; Mpourmpakis, G.; Vlachos, D. G., DFT Study of Furfural Conversion to Furan, Furfuryl Alcohol, and 2-Methylfuran on Pd(111). *ACS Catal.* **2012**, *2* (12), 2496-2504.
92. Wan, W.; Jenness, G. R.; Xiong, K.; Vlachos, D. G.; Chen, J. G., Ring-opening reaction of furfural and tetrahydrofurfuryl alcohol on hydrogen-predosed iridium(1 1 1) and cobalt/iridium(1 1 1) surfaces. *ChemCatChem* **2017**, *9* (9), 1701-1707.
93. Wang, Y. Z.; Liu, F.; Han, H.; Xiao, L. F.; Wu, W., Metal phosphide: a highly efficient catalyst for the selective hydrodeoxygenation of furfural to 2-methylfuran. *Chemistryselect* **2018**, *3* (27), 7926-7933.
94. Chen, X.; Zhang, L.; Zhang, B.; Guo, X.; Mu, X., Highly selective hydrogenation of furfural to furfuryl alcohol over Pt nanoparticles supported on g-C₃N₄ nanosheets catalysts in water. *Sci. Rep.* 2016, *6*, 28558.
95. O'Neill, B. J.; Jackson, D. H. K.; Crisci, A. J.; Farberow, C. A.; Shi, F. Y.; Alba-Rubio, A. C.; Lu, J. L.; Dietrich, P. J.; Gu, X. K.; Marshall, C. L.; Stair, P. C.; Elam, J. W.; Miller, J. T.; Ribeiro, F. H.; Voyles, P. M.; Greeley, J.; Mavrikakis, M.; Scott, S. L.; Kuech, T. F.; Dumesic, J. A., Stabilization of copper catalysts for liquid-phase reactions by atomic layer deposition. *Angew. Chem. Int. Edit.* 2013, *52* (51), 13808-13812.
96. Twigg, M. V.; Spencer, M. S., Deactivation of supported copper metal catalysts for hydrogenation reactions. *Appl. Catal. A* 2001, *212* (1-2), 161-174.
97. Bremner, J. G. M.; Keeys, R. K. F., The hydrogenation of furfuraldehyde to furfuryl alcohol and sylvan (2-methylfuran). *J. Chem. Soc.* 1947, (Aug), 1068-1080.
98. Seo, G.; Chon, H., Hydrogenation of furfural over copper-containing catalysts. *J. Catal.* 1981, *67* (2), 424-429.

CHAPTER 6

HYDROGENATION OF CINNAMALDEHYDE WITH BIMETALLIC PHOSPHIDES: EFFECT OF METAL COMPOSITION AND OBSERVATION OF PRODUCT-INDUCED REACTION MODULATION

6.1 Introduction

Chemoselective hydrogenation of α,β -unsaturated carbonyl such as cinnamaldehyde compounds is one of the important reaction in biomass upgrading as explained in the introduction Chapter. This reaction is challenging due to the competition between the hydrogenation of C=O bond and the thermodynamically favored C=C bond.¹⁻³ Since thermodynamics favor hydrogenation of the alkene, the hydrogenation of the carbonyl without reducing the C=C group is challenging. Thus, catalysts with high selectivity to COL are desired.

Many factors such as particle size⁴⁻⁸, support effects⁹⁻¹³, solvent^{12, 14-16}, and alloying¹⁷⁻²⁴ are used as strategies to tune the selectivity to COL. In several of these studies, increasing the C=O interaction to the catalyst surface is key to tuning the selectivity to COL,²³ and these interactions can be enhanced through the addition of an electropositive metal.¹⁸ For example, the selectivity to COL

using a Co catalyst can be significantly improved by adding either Ga or In, where the electropositive metals served as the C=O adsorption site.¹⁸ Similar observations have also been reported with Ru-Sn^{δ+}/ ZrO₂ catalysts.⁵

A variety of monometallic phosphides, *MP* (*M* = Mo, W, Fe, Co, Ni), have been reported as effective CAL hydrogenation catalysts for the synthesis of HCAL.²⁵ However, the addition of a second metal to form bimetallic phosphides can drastically alter the selectivity of the catalysts.²⁶ In Mo-based bimetallic systems, surface electronics can be altered, as presented in Chapter 3, by the addition of a second metal, which determines the adsorption orientation of the reactants on the surface.²⁷⁻³⁰ In Chapter 3-5, it was established that the interaction between the lone pair electrons in O and the catalyst surface is essential in facilitating the C-O or C=O bond activation.³¹⁻³⁵ The surface electronics of bimetallic phosphides can be altered further by changing the metals ratio.²⁷⁻²⁹

Herein, the catalytic performance of RuMoP was evaluated for the liquid phase hydrogenation of CAL. Metal substitution was investigated in *MMoP* (*M* = Ru, Ni, Co) to determine if any how the selectivity can be tuned from the composition. For comparison, the catalytic performance of monometallic Ni, Co, Ru, and Mo phosphides were also investigated for the hydrogenation of CAL. We discovered that surface competition between the substrates and products existed, whereby the selectivity to carbonyl reduction increased with the addition of various products. Infrared spectroscopy was used to observe and compare the adsorption of CAL on the different bimetallic catalysts. Lastly, the activation

energy barrier for H-addition was calculated using density functional theory (DFT) to validate the experimental results.

6.2 Experimental setup

6.2.1 Materials

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 81-83% MoO_3), $\text{RuCl}_3\cdot x\text{H}_2\text{O}$ (Oakwood, 67%), $(\text{NH}_4)_2\text{HPO}_4$ (VWR, 99%), citric acid monohydrate (VWR, 99%), $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 98%), $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 98-102%), cinnamaldehyde (Milipore Sigma, 98%), 2-propanol (J.T. Baker, 99%), cinnamyl alcohol (Acros Organics, 98%), benzenepropanol (Alfa Aesar, 99%), 3-phenylpropionaldehyde (Alfa Aesar, 99%), pyridine (EMD Milipore, 99%).

H_2 (Airgas, 99.999%), N_2 (Airgas, 99.999%), 1.01% O_2/He (Airgas), 30% CO/He (Airgas), 5% H_2/Ar (Airgas)

6.2.2 Catalyst synthesis

Unsupported monometallic and bimetallic phosphides were synthesized by temperature programmed reduction (TPR) as described in previous studies.³⁰

In a bimetallic phosphide synthesis, 0.7 mmol of citric acid is mixed with 0.72 mmol of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 5 mmol of $\text{RuCl}_3\cdot x\text{H}_2\text{O}$ / $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ / $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, and 5 mmol of $(\text{NH}_4)_2\text{HPO}_4$ in 25 mL of water. The mixture was calcined at 200°C for 2 h with 1°C/min temperature ramp. The dried mixture was ground into a fine powder. The calcination step was continued to 550°C with a 1°C/min ramp rate for 6 h. The resulting powder was reduced under 160 mL/min

of H₂ at 650°C for 2 h with 5°C/min ramp rate. Lastly, the reduced powder was passivated with 160 mL/min of 1% O₂/He before it was stored in the glove box. Similarly, monometallic phosphide synthesis involve the addition of citric acid (0.7 times metal content), metal precursor (Ni: Ni(NO₃)₂·6H₂O, Co: Co(NO₃)₂·6H₂O, Ru: RuCl₃·xH₂O, Mo: (NH₄)₆Mo₇O₂₄·4H₂O), and (NH₄)₂HPO₄. The monometallic phosphide synthesis follows the same calcination and reduction steps as the bimetallic phosphides.

6.2.3 Catalyst characterization

The crystal structure of the materials was confirmed using powder x-ray diffraction on a Bruker D8 Advance Davinci diffractometer. A Si (111) standard was physically mixed with the sample, and the Si (111) peak was shifted to 28.44° 2θ. The bulk composition of the material was determined using inductively coupled plasma – optical emission spectroscopy (ICP-OES; PerkinElmer Optima 8000). N₂ physisorption was used to obtain the surface area of the synthesized materials, which was collected on a Quantachrome Nova 2200e instrument. The sample was pretreated at 150°C under vacuum for at least 12 hours prior to analysis. The Brunnauer-Emmett-Teller (BET) analysis was used to calculate the surface area of the materials. The H₂ uptake for each material was quantified with H₂ temperature programmed reduction (TPR) with a Micromeritics Chemisorb unit with a thermal conductivity detector (TCD). Approximately 50 mg of the sample was pretreated with 30 mL/min Ar flow at 850°C for 1 h with 10°C/min ramp rate. After cooling the sample to 50°C, the gas flow was switched to 30 mL/min 5% H₂

in He. Lastly, the sample was heated slowly to 850°C for 1 h with a 1°C/min ramp rate. During these steps, a trap was installed before the TCD and was cooled to 77°C to prevent water contamination in the measurements.

The nature of the surface sites was probed with pyridine adsorption via diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The DRIFTS experiments were performed with a Bruker Vertex 70 with a liquid N₂ cooled mercury-cadmium-telluride (MCT). For each experiment, 80.0 mg KBr was placed in the sample cup followed by ~20.0 mg of the catalyst powder. The sample was then pressed to create a relatively flat surface. The sample was pretreated under 30 mL/min of H₂ at 400°C for 2 h. Background scans were obtained at both 100°C and 50°C under 30 mL/min of N₂ flow to appropriately examine spectra at different temperatures. Pyridine adsorption was performed at the desired temperature by flowing N₂ through a bubbler containing pyridine to contact with the catalyst surface (~ 1 h). After saturation, physisorbed pyridine on the catalyst was removed by flowing N₂ for 20 mins. A similar procedure was applied for CAL adsorption by placing CAL in the bubbler instead of pyridine.

6.2.4 Catalyst testing

All catalyst testing was completed in a custom made up-flow stainless steel reactor. The catalyst was pelletized to 60-100 mesh and was diluted 4 times with SiO₂ gel. Before the feed solution was introduced, the catalyst was pretreated at 400°C under 100 mL/min of H₂ flow for 1 h and subsequently cooled to the reaction temperature (125°C). After pressurizing the system to 4.2

MPa, liquid feed was pumped with a Hitachi L-6000 HPLC pump. For the doping study, the liquid feed was switched quickly during reaction to a separate feed reservoir containing the desired amount of the dopant. Samples were collected using a sampling port and were analyzed with an Agilent 7860A gas chromatograph – 5975 mass spectrometer (GCMS). Calibration curves were made using the reactants and products to quantify the reaction progress.

6.2.5 Computational methods

Calculations were performed through the implementation of plane wave DFT³⁶⁻³⁷ in Vienna *ab Initio* Simulation Package (VASP.5.4.4)³⁸⁻⁴³. The exchange correlations were treated within the generalized gradient approximation (GGA) by using optB88-vdW functional⁴⁴⁻⁴⁵. Projector augmented wave (PAW)⁴⁶ potentials were used to represent the effective core radii to solve the Kohn-Sham equations^{37, 47}. The electronic optimization was achieved self-consistently with a cutoff energy of 450 eV. We found that energy cutoff of 450 eV is the good cutoff for the convergence of the total energies, energy differences and structural parameters. The electronic energy convergence was set at 10^{-5} eV, the same criteria were used in previous studies. The convergence for forces during structural relaxation is set at 0.03 eV Å. Spin-polarization was included in all calculations with gamma point sampling of the Brillouin zone⁴⁸. For the structural relaxation, the first-order Methfessel-Paxton smearing⁴⁹ was employed with a σ of 0.1 eV.

The slab used for simulations, consists of three and four layers in RuMoP (112) and NiMoP (111), respectively, with a supercell size P (2 X 2) with a 15 Å thick vacuum layer in the z-direction (perpendicular to the surface) to minimize interactions between neighboring image slabs. For all calculations, the bottom most layer was fixed to represent the corresponding crystal structure obtained from DFT, whereas all other atoms were allowed to relax. The binding energy was calculated as:

$$E_{BE} = E_{\text{ADSORBATE+SURFACE}} - E_{\text{SURFACE}} - E_{\text{ADSORBATE}} \quad (\text{Equation 6.1})$$

The binding energies (denoted as E_{BE}) were calculated according to Equation 1, wherein $E_{\text{ADSORBATE+SURFACE}}$ is defined as the total energy of species adsorbed on the surface; E_{SURFACE} is defined the total energy of surface; and $E_{\text{ADSORBATE}}$ is defined as the energy of the adsorbed species on the surface in the gas phase. The activation energy barriers were defined as:

$$E_A = E_{\text{TS}} - E_{\text{IS}} \quad (\text{Equation 6.2})$$

The energy barriers were obtained by taking the difference between the energy of the transition state (E_{TS}) and its corresponding initial state (E_{IS}) as shown in Equation (2). Transition states were located using the nudged elastic band (NEB) method⁵⁰⁻⁵² and these were further refined with the climbing image

nudged elastic band (CINEB) method⁵³. The identified transition states were confirmed by examining vibrational frequencies.

6.3 Results and discussion

6.3.1 Monometallic and bimetallic phosphide screening

Monometallic and bimetallic phosphides were synthesized using a temperature programmed reduction (TPR) method described in the experimental section. The H₂ uptake during reduction was quantified using a chemisorption instrument connected to a thermal conductivity detector (Table 6.1). The TPR profiles of post-calcined precursor are plotted in Figure 6.1. From the Co₂P TPR profile, a smaller peak at 320°C from CoO_x was observed, while the Co phosphate reduction showed higher temperature peaks.⁵⁴ Similarly, the reduction of Ni₂P precursors yielded multiple H₂ consumption peaks. The peaks at 180°C and 430°C arise from bulk NiO_x reduction, while the peaks at 500-700°C is due to Ni phosphate reduction.⁵⁵⁻⁵⁶ For Ru-based metal phosphides, low temperature peaks were observed. For example, in RuP and Ru₂P, reduction events occurred between 100°C – 400°C, which were likely from reduction of the oxidic Ru after calcination.⁵⁷⁻⁶⁰ MoP reduction commenced at slightly higher temperatures than other materials (500°C) and resulted in the conversion of the MoO_x precursor to form MoP.^{58, 61} The bimetallic phosphides (CoMoP, NiMoP, and RuMoP) also displayed H₂ consumption peaks at higher temperature, which were also associated with MoO_x reduction.⁶¹ For RuMoP, the lower temperature peak at 200°C might originate from RuO_x reduction. Interestingly, the RuP, Ru₂P, and

RuMoP showed different TPR profiles due to difference in metal to P content and formation of bimetallic species.⁵⁶⁻⁵⁷ Overall, the TPR profile provided reduction temperature ranges for the materials. However, reducing the materials at higher temperature results in sintering and thus lower site density. In the case of MoP, holding the reduction temperature at 650°C for 2 h was sufficient to convert the oxidic precursor to reduced metal phosphides with defined crystal structures.⁶² Therefore, the reduction step during the synthesis was conducted at 650°C for 2 h. One exception was CoMoP whose defined crystal structure was observed after reduction at 750°C. The TPR profile of CoMoP also suggested that this material needs to be reduced at higher temperature.

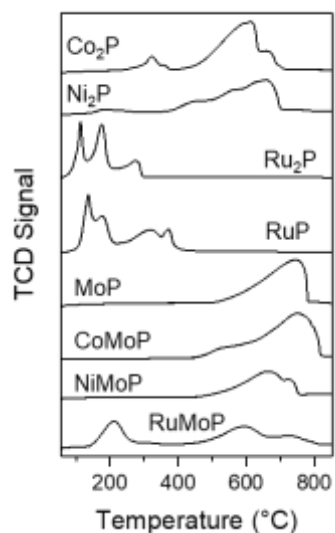


Figure 6.1. TPR profile of monometallic and bimetallic Co, Ni, Ru, and Mo phosphides.

After reduction, the crystal structures of the various phosphides were confirmed using powder XRD (Figure A.13) where the diffraction patterns matched

the respective reference data for all monometallic and bimetallic phosphides. The bulk composition was quantified with ICP-OES to show the materials are very close to the targeted bulk composition (Table S1). The BET surface area (S_{BET}) of the materials was determined with N_2 physisorption. As shown in Table S2, the surface area of the unsupported powders was in the range of 5 – 8 m^2/g , which is typical for these materials.

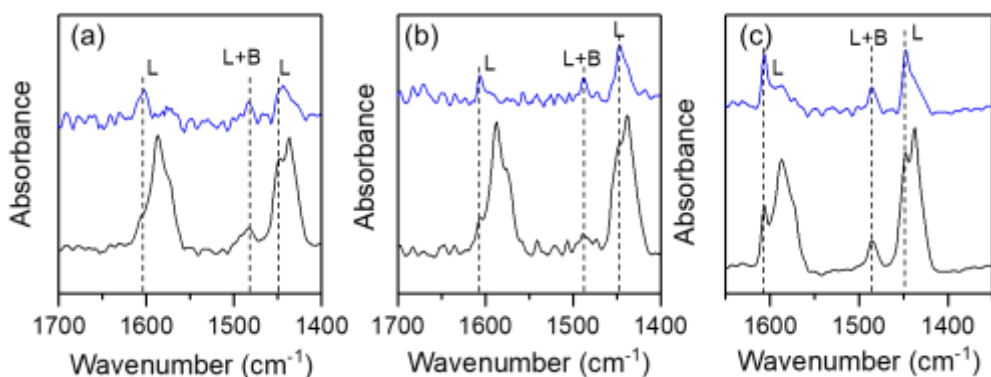
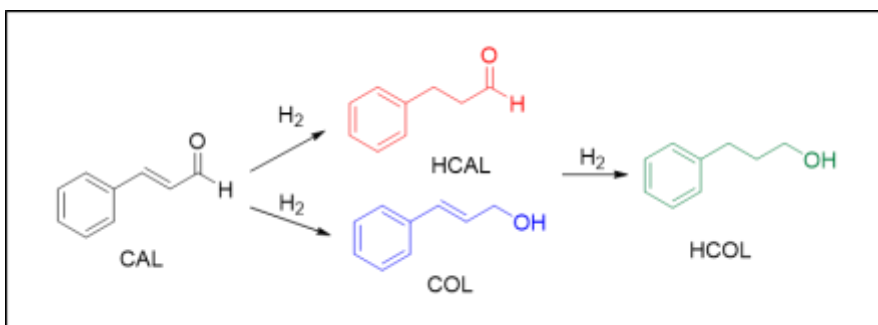


Figure 6.2. Pyridine adsorption on bimetallic (a) CoMoP, (b) NiMoP, and (c) RuMoP under DRIFT spectroscopy at pyridine saturation (black) and after N_2 purging (blue).

Pyridine adsorption was performed using DRIFTS to determine the nature of acid site of the materials. Pyridine can interact directly with Lewis acids or is protonated by a Brønsted acid to provide different ring vibration modes.⁶³⁻⁶⁴ The pyridine adsorption modes on bimetallic CoMoP, NiMoP, and RuMoP are presented in Figure 6.2 a-c with the pyridine saturated surface represented in black and the N_2 purged surface in blue. For the pyridine saturated surface, features at 1590 cm^{-1} and 1430 cm^{-1} are assigned to physisorbed pyridine.⁶⁴ These features decreased in intensity upon purging with N_2 . The remaining three

features after flowing N_2 were assigned to chemisorbed pyridine on Lewis and Brønsted acid sites. The features at 1604 cm^{-1} and 1448 cm^{-1} are assigned to ν_{8a} and ν_{19b} adsorption mode on Lewis sites (e.g., electron deficient site or partially oxidized metal).⁶³⁻⁶⁵ Meanwhile, the feature at 1485 cm^{-1} was assigned to coordinated pyridine on either or both Lewis and Brønsted acid sites. However, the Brønsted acid interaction with pyridine yields a feature at 1550 cm^{-1} , which was not observed in any of the bimetallic phosphides. Therefore, the predominant acid sites in these bimetallic phosphides have Lewis acidic character. The same analysis was also performed on monometallic Co_2P , Ni_2P , Ru_2P , RuP , and MoP (Figure A.15). These materials provided the same features as the bimetallic phosphide after pyridine adsorption. The observation agreed with previous reports using pyridine adsorption to probe the acidity of metal phosphides.⁶⁵⁻⁶⁶



Scheme 6.1. Reaction pathway of CAL hydrogenation

The catalytic performance of monometallic and bimetallic phosphides was investigated for CAL hydrogenation at 125°C and 4.2 MPa . Initially, hydrogenation of CAL can occur on either the $C=C$ group or the $C=O$ group

forming HCAL or COL, respectively (Scheme 1). The subsequent hydrogenation of HCAL and COL results in HCOL (Scheme 1).

Although the catalytic performance of monometallic phosphides for CAL hydrogenation has been previously investigated in other studies,²⁵ we evaluated various monometallic phosphides to directly compare the results of all materials in this study under the same reaction conditions and conversions. The monometallic MoP, CoP, Ni₂P, RuP, and Ru₂P catalysts were tested in a flow reactor at 125°C and 4.2 MPa H₂ according to the procedure described in the experimental section. The reaction results are summarized in Table 6.1. First, Co₂P was tested since a previous report showed that Co₂P/SiO₂ has the highest selectivity to COL.²⁵ However, according to our result Co₂P is highly selective (99-95%) to C=C bond hydrogenation to form HCAL at 5% and 20% conversion. There are many possible reasons for these differences such as difference in crystal structures, elemental composition, support effects, and solvent. However, due to the lack of information in crystal structures and elemental composition from the previous study, it is challenging to determine the cause.²⁵ Ni₂P also showed high selectivity to HCAL, which agreed with the previous report, which could possibly exclude support and solvent choices from the discrepancies seen in Co₂P.²⁵ Similarly, Ru₂P was investigated and provided a selectivity to HCAL of 88% at 5% conversion. At a higher conversion of 75%, the selectivity to HCAL decreased to 69% while the subsequent hydrogenation to HCOL increased to 24%. Meanwhile, the

selectivity to COL with RuP was found to be 31% at 4% conversion, which decreased to 21% at higher conversion of 27%. MoP was also tested since our previous study suggested that the Lewis acidic Mo site interacts with the oxygenated compounds.²⁸ At low conversion of 6%, the selectivity to COL was 26%, which agreed with previous report.²⁵ However, at a higher conversion of 20%, the selectivity to COL increased significantly to 77%.

TABLE 6.1.
CATALYTIC PERFORMANCE OF MO, CO, NI, AND RU MONOMETALLIC
PHOSPHIDES AT 125°C AND 4.2 MPA

	X (%)	S _{COL} (%)	S _{H₂CAL} (%)	S _{H₂COL} (%)
Co ₂ P	5	0	99	0
	20	0	95	5
Ni ₂ P	19	0	98	2
	92	1	97	2
Ru ₂ P	5	7	88	5
	75	7	68	25
RuP	4	31	69	0
	27	21	75	4
MoP	5.8	26	73	1
	20	77	20	3

To improve the COL selectivity that resulted from MoP, we considered a few bimetallic Mo-based phosphides since charge transfers between the elements could improve the surface-O interaction.^{5, 13, 17-18, 67} Similarly, the same strategy is implemented to monometallic MoP where metal addition has been shown to alter the relative oxidation or Lewis acid character of the Mo metal

studied through x-ray photoelectron spectroscopy (XPS), x-ray absorption near edge spectroscopy (XANES), and Bader charge calculation.²⁸⁻³⁰ RuMoP was of interest because Ru (along with P) accepts electrons from Mo and becomes partially negative while the Mo atom is partially positive.^{30, 68} Additionally, CoMoP and NiMoP were studied since these metals can also participate in charge transfer, although these materials result in less Lewis acid character for Mo.²⁸⁻²⁹

The three bimetallic phosphides mentioned above (CoMoP, NiMoP, and RuMoP) were tested for CAL hydrogenation. The results are plotted in Figure A.16 and Figure 6.3 for CoMoP, NiMoP, and RuMoP, respectively. The CoMoP catalyst (Figure A.16) showed a high selectivity (99 –92%) to HCAL at conversion ranging from 3 – 30%. The NiMoP catalyst (Figure 6.3a) showed initial high selectivity to C=C bond hydrogenation to form HCAL. However, at longer residence times, the selectivity to HCOL increased. In comparison with the monometallic phosphides, Mo addition to Co phosphide did not produce a bimetallic effect since no improvement in selectivity was observed. Meanwhile, Mo addition to Ni phosphide increased the selectivity to HCOL, although hydrogenation of the C=C remained the dominant initial pathway. Other reports have observed increased Mo-O interactions with bimetallic NiMoP compared to monometallic Ni₂P.⁶⁹ These effects were attributed to electronic effects associated with the charge transfer from Mo to Ni and P, which lowered the electron density of Mo to become more oxophilic.⁶⁹⁻⁷⁰

RuMoP showed a different selectivity compared to the other two catalysts. At the lowest residence time, the selectivity was 74% to COL, 24% to HCAL, and

2% to HCOL (Figure 6.3b). As the reaction progressed, the selectivity towards COL increased to 91% at 43% conversion. The differences in C=C and C=O hydrogenation preferences were probed further with DFT calculations for RuMoP and NiMoP.

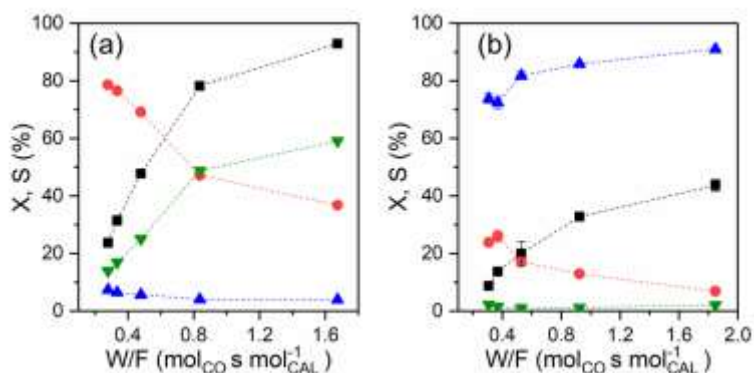


Figure 6.3. Conversion (X – black) and selectivity (S) of COL (blue), HCAL (red), and HCOL (green) as a function of W/F for (a) NiMoP and (b) RuMoP.

The relaxed binding configurations of the reactant (CAL) and products (COL, HCAL, and HCOL) on RuMoP and NiMoP surfaces are shown in Figure 6.4. CAL binding on both RuMoP and NiMoP surfaces are favorable evident by their binding energy of -2.24 eV and -2.02 eV, respectively. However, CAL binds in a different orientation on RuMoP and NiMoP surfaces. The binding modes of CAL on RuMoP and NiMoP were deciphered through the partial atomic charge transfers (Table S5) and distances (Table S6) post CAL binding. These results indicated that the distance of the carbonyl O atom referred as O₁ in RuMoP is closer to the surface (1.94 Å) compared to on NiMoP surface (3.85 Å). Moreover, the partial atomic of the O₁ atom is 0.35 and 0.30 |e| for RuMoP and NiMoP respectively, which indicates higher charge transfer to the O₁ atom from the RuMoP surface.

Meanwhile, the atomic charges of the carbonyl C (C_1) and α -C (C_2) were very similar and within 0.02 |e| difference. However, the partial atomic charge of the β -C (C_3) is higher in NiMoP (0.34 |e|) compared to RuMoP (0.12 |e|). Further, the C_3 atom to the surface distance is lower in NiMoP (2.51 Å) than RuMoP (2.84 Å) surface. The result suggests that charge transfer occurs more favorably to the O_1 atom on RuMoP and C_3 atom on NiMoP, which might account for the C=O and C=C selectivity, respectively.

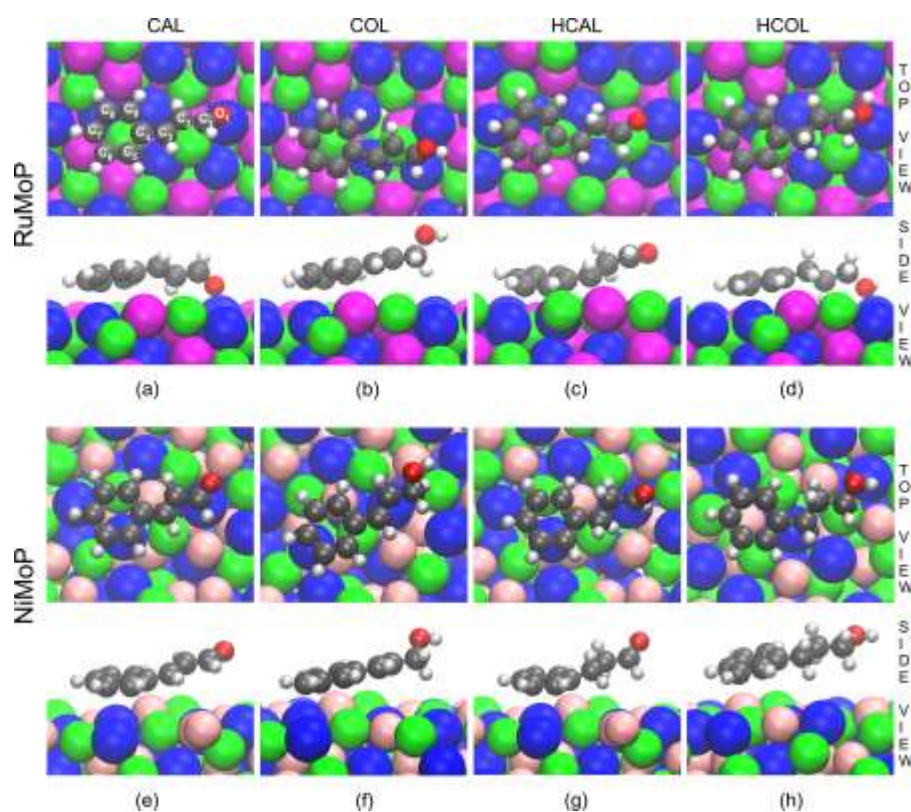


Figure 6.4. Optimized structures of CAL, COL, HCAL, and HCOL on RuMoP (112) (a-d) and NiMoP (111) (e-h) (purple for Ru; pink for Ni; blue for Mo; green for P; grey for C; silver for H; red for O).

NiMoP showed selectivity shifts from HCAL to HCOL indicating further

saturation of the C=O bond in HCAL. Indeed, computational calculation suggests there are charge transfers to the C₁ and O₁ atoms evident by the partial atomic charges of 0.15 |e| and 0.12 |e|, respectively in HCAL over NiMoP. This observation is the opposite of RuMoP where the partial atomic charge transfer is smaller on C₁ (0.07 |e|) and O₁ (0.05 |e|) in HCAL. Additionally, change in the partial atomic charge of C₂ (0.02 |e|) and C₃ (0.09 |e|) atoms in COL on RuMoP surface is small in comparison to NiMoP (1.41 and 1.56|e| for C₂ and C₃, respectively). The lack of charge transfer from RuMoP surface to COL and HCAL account for the high COL selectivity with minimal subsequent hydrogenation in RuMoP.

Regardless, interesting trend was observed where at higher residence times with NiMoP, the hydrogenation of the unconjugated C=O bond becomes favorable. With RuMoP, however, hydrogenation of the conjugated C=O becomes more favorable at high residence times. This result could imply that surface effects associated with surface crowding of reactive intermediates and products influence the selectivity. Therefore, further experiments were performed to study the effect of dopants on the COL selectivity.

6.3.2 Modulation study with dopants

Various dopants were investigated to modulate the catalyst selectivity by switching the feed stream with one containing a different composition of reactive species. The first modulation experiment was performed with COL as a dopant since it is the most dominant product observed during the reaction of CAL with RuMoP (Figure 6.5a). The experiment was started with a fresh feed to CAL to

establish an initial steady state baseline to observe any noticeable effects from the additives. After steady state was achieved at 8% conversion and 76% selectivity to COL, the feed was switched to 95%:5% CAL:COL while keeping the total concentration at 0.10 M. Because COL is also a product, the added amount was assumed unreactive. Therefore, the difference between the final COL amount in the outlet and the COL in the initial feed was attributed to the produced COL. The assumption that COL is unreactive is verified from experiments using it as a feed, which showed less than < 2% COL converted under similar conditions. When COL is added in 95%:5% ration, the selectivity to COL increased to ~90%. When the COL concentration was increased to 25% or 50%, the selectivity to COL remained at 91%. At 50% COL concentration, the conversion slightly increased due to the lower content of CAL in the feed. At the end of the run, the feed was switched back to the original CAL composition without added dopant and both selectivity and conversion were recovered to the steady state value (Figure 6.5a). The results suggested that COL interacts with the surface to modulate the selectivity of CAL to COL. This is likely the reason the COL selectivity increased over RuMoP as a function of W/F.

The same doping experiment was performed with NiMoP. It could be seen that the selectivity to COL increased as the concentration of COL dopant in the feed was increased. At a 50:50 CAL:COL ratio, the selectivity of COL was increased to 28% compared to when no COL dopant was added (11%). However, adding COL could not increase the selectivity of COL significantly on NiMoP to match that of RuMoP. Two possible explanations of the results were (1) the high COL selectivity

on RuMoP originated from the surface properties (i.e., electronics) rather than solely from surface competition effect or (2) the possibility of competition with other surface species such as HCOL and COL.

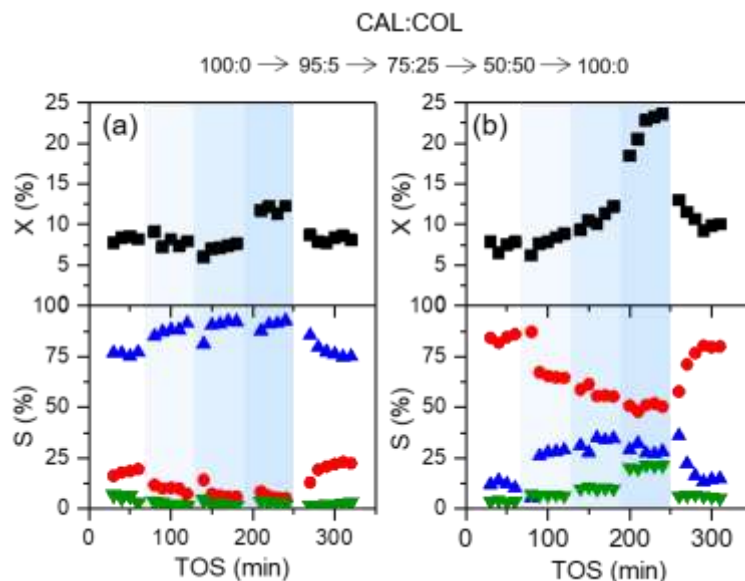


Figure 6.5. COL doping experiments with (a) RuMoP and (b) NiMoP. Temperature: 125°C, pressure: 4.2MPa, total concentration: 0.10 M.

A similar study was conducted using HCOL as a dopant rather than COL on RuMoP and NiMoP (Figure 6). The same assumption was made that the differences in HCOL between the inlet and outlet is due to HCOL formation during reaction. Since the yield to HCOL is lower than COL with RuMoP, the doping experiment was performed with a lower HCOL:CAL ratio. At 99.5:0.5 CAL:HCOL, the selectivity to COL increased to 91% COL, showing that HCOL also aided in the production of COL. The HCOL amount was increased up to CAL:HCOL of 98:2, but the selectivity remained at ~91% COL. Finally, the initial

selectivity was recovered when the feed was switched to CAL without HCOL dopant.

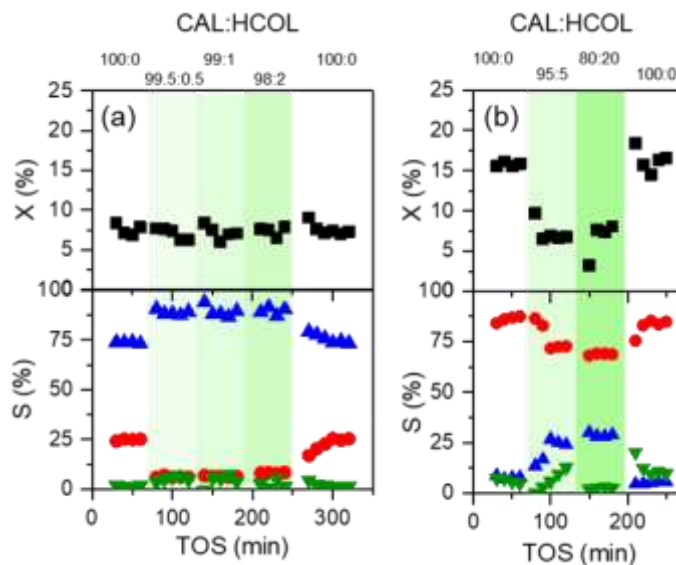


Figure 6.6. HCOL doping on (a) RuMoP and (b) NiMoP. Temperature: 125°C, Pressure: 4.2MPa, Total concentration: 0.10 M.

HCOL doping was also performed on NiMoP catalyst to determine if the doping technique can be used to tune the selectivity in NiMoP. At CAL:HCOL of 95:5, the COL selectivity increased from 9% to 30%. However, the selectivity could not be significantly improved even at 50:50 CAL:HCOL feed ratio. These results show that the products could influence the COL selectivity, but the catalyst composition (i.e., RuMoP) was essential in achieving > 90% COL selectivity.

The hypothetical surface interactions possible between CAL, COL, and HCOL are depicted in Scheme 3a, where π - π stacking of the adsorbed molecules occurs with excess COL or HCOL, forcing CAL to bind through the carbonyl O on RuMoP. In this configuration, the π - π stacking may stabilize the

C=O adsorption on the catalyst surface. This concept is similar to self-assembled monolayer (SAM) where functionalized thiols are used to create sterics on the surface to force C=O adsorption similar to our observation⁷¹. Similar concepts have also been tested on Ni₂P functionalized with p-fluorothiols, where the p-fluorothiol functionalized Ni₂P showed an increase to COL production to almost 100%.⁷² The increase in selectivity to COL was attributed to downshift in the d-band center after p-fluorothiols functionalization that increased H₂ adsorption and prevented the C=C bond from adsorbing on the active sites.⁷² Although the SAM concept has been shown to improve the C=O adsorption, these methods required the use of thiol-containing components that could potentially leach to the outlet stream. However, here we show that the products alone in combination with RuMoP can be used to create the same effect as the SAM and possible with a recycle stream incorporated to the reactor.



Scheme 6.2. (a) Possible stacking interactions between CAL, COL, and HCOL on the RuMoP and NiMoP surface and (b) possible surface interactions with both CAL and pyridine⁷³

A poisoning experiment was performed since pyridine has been shown to stabilize CAL adsorption through the carbonyl O on a Pd/C surface by forming a

H-bond with the α -H on pyridine (Scheme 2b).¹ The poisoning experiment was also performed on both RuMoP (Figure 7a) and NiMoP (Figure 7b). As noted previously in Figure 2, pyridine adsorption on these catalysts occurs predominantly through Lewis acidic sites, and the addition of pyridine to the reaction feed could block these sites. The experiment was initially started with a fresh, pretreated catalyst and CAL with no pyridine to obtain steady state. As expected for RuMoP, the selectivity was predominantly COL with conversion of ~6%. Upon 0.01 M pyridine doping, the conversion decreased to ~4% likely due to site blocking by pyridine, which implied that the hydrogenation site is acid site. The surface interaction with pyridine could also be observed from the increase in selectivity of COL to ~92% from ~78%, which indicates possible C=O adsorption stabilization through H-bond formation as illustrated in Scheme 2b.¹ The conversion could not be recovered to its initial value after pyridine is removed, which is due to a strong interaction between pyridine and RuMoP due to stronger Lewis acid character for this catalyst.³³ For NiMoP, the COL selectivity starts at ~10% with no pyridine at a ~21% conversion. When 0.01 M pyridine was added, a slight decrease in conversion from an average of 21% to 17% was observed, and the selectivity to COL also increased to 40%. The pyridine concentration was further increased to 0.05 M. At this point, the CAL conversion dropped drastically to an average of 4% accompanied by an increase in COL selectivity to 50%. Lastly after the feed was switch to CAL with no pyridine, the conversion could be recovered to average of 22%. Interestingly, the selectivity to HCAL increased to 97% from the original 81%. This increase is mainly from the decrease in COL formation rather than increase

of HCAL formation. This indicates that some pyridine might be left on the catalyst surface and could not be flushed within 60 mins. The result also suggests that the leftover pyridine was blocking specifically sites that produces COL.

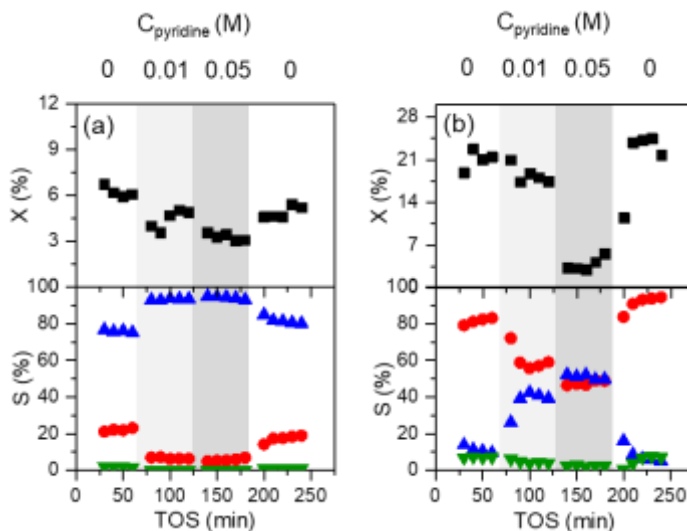


Figure 6.7. Pyridine doping during 0.10 M CAL hydrogenation on (a) RuMoP and (b) NiMoP with pyridine.

6.3.3 CAL surface interaction

The surface interaction between CAL and the different catalysts was studied with DRIFTS under an inert atmosphere (N_2) and under a reactive gas environment (H_2). The experiments were performed according to the procedural steps described in section 2.3 with a H_2 pretreatment step followed by substrate saturation through a N_2 bubbler and N_2 purging to remove physisorbed substrates.

The spectrum for the adsorption of CAL on RuMoP under N_2 after the removal of physisorbed CAL is plotted in Figure 6.8a. Two distinct peaks at 1680 cm^{-1} and 1624 cm^{-1} are assigned to the $\nu(C=O)$ and $\nu(C=C)$ vibrations.^{18, 73-74} The

peak locations were red-shifted from the gas phase values suggesting interaction between CAL and the catalyst surface.⁷⁴ The flow of N₂ was switched to H₂ flow to observe the change in C=O and C=C surface interactions under H₂ flow. The spectrum was taken at 50°C instead of the reaction temperature 125°C to decrease the rate at which the peak disappeared. After H₂ was introduced into the cell, spectra were obtained every 2000 s. These spectra are reflected in Figure 6.8a in red, blue, and purple, respectively with decreasing intensity as reaction time progresses indicating the reacted species are leaving the surface.

CAL adsorption was also performed on NiMoP (Figure 6.8b). The adsorption of CAL on NiMoP (black curve) generated more IR features compared to RuMoP. The C=C bond feature in NiMoP was observed at similar location as in RuMoP at 1626 cm⁻¹. However, two C=O features were observed at 1690 cm⁻¹ and 1672 cm⁻¹.⁷⁴ The assignment of these C=O features are difficult due to the many proposed binding configuration of C=O such as $\eta_1(\text{O})$, $\eta_2(\text{C-O})$, π -bonded (C=O), acyl-type adsorption, and 1,4-diadsorbed species (Figure A.17).⁵¹ The $\eta_1(\text{O})$ configuration adsorbs on the catalyst surface through the O atom that leads to the C=O bond hydrogenation.⁷⁵ This is likely the configuration that is observed on RuMoP since C=O bond hydrogenation to form COL is the dominant product. In NiMoP, C=C bond hydrogenation to form HCAL is the main product. Therefore, configurations other than $\eta_1(\text{O})$ exists on NiMoP. The $\eta_2(\text{C-O})$ and acyl- type adsorption mode has been reported to be related to the C-O bond cleavage in aldehyde-type adsorbates.⁷⁶⁻⁷⁷ Since C-O bond cleavage is not observed in this work, the $\eta_2(\text{C-O})$ and acyl-type adsorption can be eliminated.

The π -bonded (C=O) is resistant to reaction with H_2 and have been observed to yield IR features near the $\eta_1(O)$ features about 50 cm^{-1} upshifted similar to adsorption on NiMoP and thus this mode of adsorption is possible on NiMoP.⁷⁸

Similar to the RuMoP experimental setup, H_2 was flowed into the system and spectra were collected every 2000 s shown in red, blue, and purple, respectively (Figure 6.8b). The C=C feature was shown to decrease over reaction time due to hydrogenation of the C=C bond. The C=O feature at 1690 cm^{-1} seemed to decrease slightly, but the C=O feature at 1672 cm^{-1} decreased at a higher rate. Since the feature on 1690 cm^{-1} is resistant to H_2 addition, it is possible that this feature belongs to the π -bonded (C=O), while the 1672 cm^{-1} is assigned to $\eta_1(O)$ adsorption. This decrease in C=O was possibly due to loss in conjugation after the C=C bond was hydrogenated followed by product desorption.⁷⁴ Another possible C=O adsorption is through the 1,4-diadsorbed mode as has been proposed through theory.⁷⁹ In this mode of adsorption, the O_1 and C_3 both adsorbed on the catalyst surface either on one active sites or two active sites. This mode of adsorption leads to virtually no C=O bond hydrogenation.⁷⁹ Referring back to the partial atomic charge result from CAL adsorption (Table S5), the charge transfer from the NiMoP catalyst surface is the highest on both O_1 and C_3 position (0.30 and 0.34 |e|), which could imply that CAL adsorbed through the O_1 and C_3 position in the 1,4-diadsorbed mode.

Nevertheless, the DRIFT spectra provided evidence of the $\eta_1(O)$ adsorption mode in RuMoP is essential for the hydrogenation of C=O bond. DFT calculation also confirmed that the charge transfer from the RuMoP surface is

mostly through the O₁ atom. On the other hand, $\eta_1(\text{O})$ adsorption mode is not the predominant adsorption mode in NiMoP with potential π -bonded C=O or 1,4 diadsorbed contributing to the hydrogenation of C=C bond.

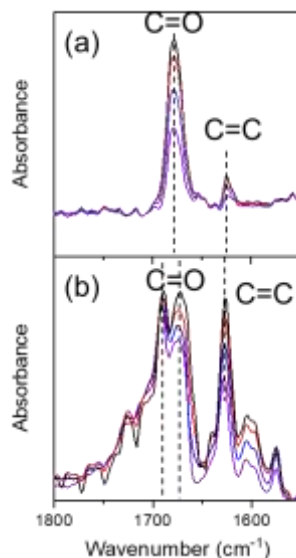


Figure 6.8. Cinnamaldehyde adsorption on (a) RuMoP and (b) NiMoP at saturation (black) in N₂ flow followed by H₂ flow for 2000 s (red), 4000 s (blue), and 6000 s (purple).

6.3.4 Computational results

Density functional theory (DFT) calculation was performed to gain theoretical insight of CAL hydrogenation on RuMoP and NiMoP. The DFT results showed preferential first hydrogenation step of C=O bond on RuMoP and C=C bond on NiMoP in the presence of surface adsorbed hydrogens. According to the results, here are 4 possible atom locations for the first H-addition: (1) O₁ or (2) C₁ for the hydrogenation of C=O bond and (3) C₂, or (4) C₃ for the hydrogenation of C=C bond as shown in Figure 6.8a-b. Further, atom nomination has shown in Figure 6.4. The activation energy (E_A) was calculated for the first and second H-

addition on position 1 to 4 and its following H-addition as described in Figure 6.9a and b for RuMoP and NiMoP, respectively. Pathway I and II denote the H-addition on O₁ followed by C₁ and C₁ followed by O₁, respectively. Both pathways I and II yield COL as the final product. Pathway III and IV showed H-addition on C₂ followed by C₃ and its reverse respectively, leading to HCAL formation. These hydrogenation reactions start in the presence of surface adsorbed hydrogen atoms, and the most stable binding site is determined as on the top of Mo as discussed in our past studies.^{29, 66}

The transition state energy of each elementary step for the proposed reaction pathway I-IV was calculated on RuMoP(112) and NiMoP(111) as the most dominant facet seen in XRD. Pathway I and II are initiated by binding of CAL in the presence of two surface adsorbed H-atoms as shown in Figure A.18a and f, respectively. This step leads the formation of (C₆H₅)C₂H₂CHOH* and (C₆H₅)C₂H₂CH₂O* (INT1) due to addition of one H to the O₁ and C₁ atom as shown in Figure A.18c and h with the $E_{BE} = -2.03$ and -1.93 eV (See Figure 6.9a) for pathway I and II, respectively. The transition state (TS1) for this step has shown in Figure A.18b and g with the E_A of 0.35 and 0.70 eV for pathway I and II, respectively. This result indicates that pathway I (H-addition on O₁) is more favorable on RuMoP, possibly due to the close proximity of O₁ on RuMoP surface as well as higher charge transfer to O₁ from the catalyst surface as mentioned in the previous section. The formed intermediate is further hydrogenated to COL ((C₆H₅)C₂H₂CH₂OH*) as shown in Figure A.18e and j and transition state (TS2) related to the second hydrogenation step has been shown in Figure A.18d and i

for pathway I and II, respectively. The E_A for TS2 for pathway I and II are 0.68 and 0.65 eV.

Pathway III and IV were also evaluated on RuMoP(112) for the formation of $(C_6H_5)CHCH_2CHO^*$ and $(C_6H_5)CH_2CHCHO^*$ intermediate at TS1, respectively as shown in Figure A.18m and r. The binding energy for these steps are -2.11 and -2.07 eV. Further, this intermediate goes for another hydrogenation step in the presence of second surface adsorbed H atom. This leads the final product formation HCAL as shown in Figure A.18o and t and TS2 related to this step has been shown in Figure A.18n and s for pathway III and IV, respectively. The E_A for TS1 of pathway III and IV on RuMoP(112) are 0.48 and 0.51 eV, while the E_A for TS2 are 0.71 and 0.83 eV. The lowest E_A for TS1 and overall E_A was still through pathway I, which suggested that the first H-addition in RuMoP was more favorable through the C=O bond as evident by the high COL formation seen experimentally.

Similarly, the same analysis on E_A of TS1 and TS2 for pathway I to IV were performed on NiMoP(111) (Figure A.19). The E_A of the first H-addition step or TS1 for pathway I, II, III, and IV were 0.61, 0.89, 0.39, and 0.26 eV (See Figure A.19b). The lowest E_A for the first H-addition in pathway IV implied that the most favorable H-addition was on the C_3 position $> C_2 > O_1 > C_1$. The E_A for TS2 for pathway I, II, III, and IV were 0.78, 0.95, 0.68, and 0.57 eV, respectively. Although the first H-addition was favorable through pathway IV, second H-addition was preferable to pathway III. Overall, pathway III and IV compete for

C=C bond hydrogenation to form HCAL due to lower E_A in NiMoP which agreed with the experimental observation.

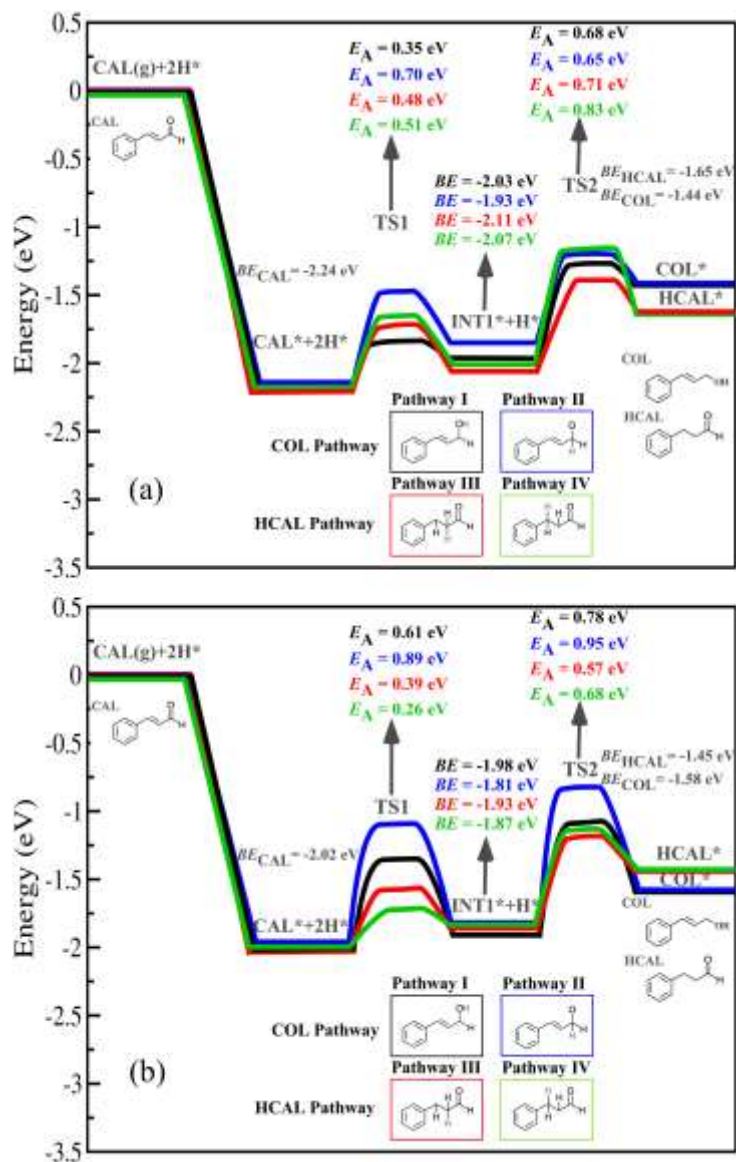


Figure 6.9. Cinnamaldehyde adsorption on (a) RuMoP and (b) NiMoP at saturation (black) in N₂ flow followed by H₂ flow for 2000 s (red), 4000 s (blue), and 6000 s (purple).

6.4 Conclusion

The selectivity of C=O and C=C bond hydrogenation in α,β -unsaturated aldehyde such as CAL can be tuned with monometallic and bimetallic phosphides. Monometallic phosphides such as Ni₂P, Co₂P, RuP, Ru₂P were highly selective towards C=C bond hydrogenation with 99% selectivity achieved with Ni₂P and Co₂P catalysts. Monometallic MoP showed C=C bond hydrogenation preference at low conversion, but the selectivity shifts to C=O at higher conversion. Bimetallic RuMoP was able to increase the selectivity of C=O bond hydrogenation to 91% in contrast with other bimetallic such as NiMoP and CoMoP. Modulation study with COL and HCOL doping suggested that the high selectivity of C=O bond hydrogenation in RuMoP was due to surface competition between the products (HCOL and COL) that created possible π - π stacking and stabilizes CAL adsorption through C=O. DRIFTS experiments of CAL adsorption showed the presence of $\eta_1(\text{O})$ adsorption mode in RuMoP that leads to the hydrogenation of C=O bond, while NiMoP showed $\eta_1(\text{O})$ adsorption mode and potential π -bonded C=O or 1,4-diadsorbed species that inhibited the hydrogenation of C=O bond. Lastly, DFT calculations indicated that H₂ addition is more favorable on C=O bond on RuMoP. Specifically, the first H-addition was more favorable on the O₁ atom. The surface electronics of RuMoP (i.e., Lewis acid character) greatly influenced the proximity of O₁ during adsorption.

6.5 References

1. Wu, L.; Moteki, T.; Gokhale, Amit A.; Flaherty, David W.; Toste, F. D., Production of fuels and chemicals from biomass: Condensation reactions and beyond. *Chem* **2016**, *1* (1), 32-58.

2. Garrote, G.; Cruz, J. M.; Moure, A.; Domínguez, H.; Parajó, J. C., Antioxidant activity of byproducts from the hydrolytic processing of selected lignocellulosic materials. *Trends in Food Science & Technology* **2004**, *15* (3), 191-200.
3. Margellou, A.; Triantafyllidis, K. S., Catalytic transfer hydrogenolysis reactions for lignin valorization to fuels and chemicals. *Catalysts* **2019**, *9* (1), 43.
4. Plomp, A. J.; Vuori, H.; Krause, A. O. I.; de Jong, K. P.; Bitter, J. H., Particle size effects for carbon nanofiber supported platinum and ruthenium catalysts for the selective hydrogenation of cinnamaldehyde. *Applied Catalysis A: General* **2008**, *351* (1), 9-15.
5. Coq, B.; Kumbhar, P. S.; Moreau, C.; Moreau, P.; Warawdekar, M. G., Liquid-phase hydrogenation of cinnamaldehyde over supported ruthenium catalysts - influence of particle-size, bimetallics and nature of support. *J. Mol. Catal.* **1993**, *85* (2), 215-228.
6. Galvagno, S.; Capannelli, G.; Neri, G.; Donato, A.; Pietropaolo, R., Hydrogenation of cinnamaldehyde over Ru/C catalysts: effect of Ru particle size. *J Mol Catal* **1991**, *64* (2), 237-246.
7. Taylor, M. J.; Durndell, L. J.; Isaacs, M. A.; Parlett, C. M. A.; Wilson, K.; Lee, A. F.; Kyriakou, G., Highly selective hydrogenation of furfural over supported Pt nanoparticles under mild conditions. *Appl. Catal. B* **2016**, *180*, 580-585.
8. Jiang, F.; Cai, J.; Liu, B.; Xu, Y.; Liu, X., Particle size effects in the selective hydrogenation of cinnamaldehyde over supported palladium catalysts. *Rsc Adv* **2016**, *6* (79), 75541-75551.
9. Toebes, M. L.; Zhang, Y.; Hájek, J.; Alexander Nijhuis, T.; Bitter, J. H.; Jos van Dillen, A.; Murzin, D. Y.; Koningsberger, D. C.; de Jong, K. P., Support effects in the hydrogenation of cinnamaldehyde over carbon nanofiber-supported platinum catalysts: characterization and catalysis. *J. Catal.* **2004**, *226* (1), 215-225.
10. da Silva, A. B.; Jordão, E.; Mendes, M. J.; Fouilloux, P., Effect of metal-support interaction during selective hydrogenation of cinnamaldehyde to cinnamyl alcohol on platinum based bimetallic catalysts. *Applied Catalysis A: General* **1997**, *148* (2), 253-264.
11. Handjani, S.; Marceau, E.; Blanchard, J.; Krafft, J.-M.; Che, M.; Mäki-Arvela, P.; Kumar, N.; Wärnå, J.; Murzin, D. Y., Influence of the support composition and acidity on the catalytic properties of mesoporous SBA-15,

- Al-SBA-15, and Al₂O₃-supported Pt catalysts for cinnamaldehyde hydrogenation. *J. Catal.* **2011**, 282 (1), 228-236.
12. Hájek, J.; Kumar, N.; Mäki-Arvela, P.; Salmi, T.; Murzin, D. Y.; Paseka, I.; Heikkilä, T.; Laine, E.; Laukkanen, P.; Väyrynen, J., Ruthenium-modified MCM-41 mesoporous molecular sieve and Y zeolite catalysts for selective hydrogenation of cinnamaldehyde. *Applied Catalysis A: General* **2003**, 251 (2), 385-396.
 13. Malobela, L. J.; Heveling, J.; Augustyn, W. G.; Cele, L. M., Nickel–cobalt on carbonaceous supports for the selective catalytic hydrogenation of cinnamaldehyde. *Ind. Eng. Chem. Res.* **2014**, 53 (36), 13910-13919.
 14. Dai, Y.; Gao, X.; Chu, X.; Jiang, C.; Yao, Y.; Guo, Z.; Zhou, C.; Wang, C.; Wang, H.; Yang, Y., On the role of water in selective hydrogenation of cinnamaldehyde to cinnamyl alcohol on PtFe catalysts. *J. Catal.* **2018**, 364, 192-203.
 15. Hájek, J.; Kumar, N.; Mäki-Arvela, P.; Salmi, T.; Murzin, D. Y., Selective hydrogenation of cinnamaldehyde over Ru/Y zeolite. *Journal of Molecular Catalysis A: Chemical* **2004**, 217 (1), 145-154.
 16. Chatterjee, M.; Ikushima, Y.; Zhao, F., Completely selective hydrogenation of trans-cinnamaldehyde to cinnamyl alcohol promoted by a Ru–Pt bimetallic catalyst supported on MCM-48 in supercritical carbon dioxide. *New Journal of Chemistry* **2003**, 27 (3), 510-513.
 17. Cattaneo, S.; Freakley, S. J.; Morgan, D. J.; Sankar, M.; Dimitratos, N.; Hutchings, G. J., Cinnamaldehyde hydrogenation using Au–Pd catalysts prepared by sol immobilisation. *Catal. Sci. Technol.* **2018**, 8 (6), 1677-1685.
 18. Yang, Y. S.; Rao, D. M.; Chen, Y. D.; Dong, S. Y.; Wang, B.; Zhang, X.; Wei, M., Selective hydrogenation of cinnamaldehyde over Co-based intermetallic compounds derived from layered double hydroxides. *Acs Catalysis* **2018**, 8 (12), 11749-11760.
 19. Pârvulescu, V. I.; Pârvulescu, V.; Endruschat, U.; Filoti, G.; Wagner, F. E.; Kübel, C.; Richards, R., Characterization and catalytic-hydrogenation behavior of SiO₂-embedded nanoscopic Pd, Au, and Pd–Au alloy colloids. *Chemistry – A European Journal* **2006**, 12 (8), 2343-2357.
 20. Ashokkumar, S.; Ganesan, V.; Ramaswamy, K. K.; Balasubramanian, V., Bimetallic Co–Ni/TiO₂ catalysts for selective hydrogenation of cinnamaldehyde. *Research on Chemical Intermediates* **2018**, 44 (11), 6703-6720.

21. Narasimhan, C. S.; Deshpande, V. M.; Ramnarayan, K., Selective hydrogenation of α,β -unsaturated aldehydes to unsaturated alcohols over mixed ruthenium–tin boride catalysts. *Journal of the Chemical Society, Chemical Communications* **1988**, (2), 99-100.
22. Zheng, Q.; Wang, D.; Yuan, F.; Han, Q.; Dong, Y.; Liu, Y.; Niu, X.; Zhu, Y., An effective Co-promoted platinum of Co–Pt/SBA-15 catalyst for selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. *Catal. Lett.* **2016**, 146 (8), 1535-1543.
23. Chen, Y. Z.; Wei, S. W.; Wu, K. J., Effect of promoter on selective hydrogenation of α,β -unsaturated aldehydes over cobalt borides. *Applied Catalysis A: General* **1993**, 99 (2), 85-96.
24. Samant, P. V.; Pereira, M. F. R.; Figueiredo, J. L., Mesoporous carbon supported Pt and Pt–Sn catalysts for hydrogenation of cinnamaldehyde. *Catal. Today*. **2005**, 102-103, 183-188.
25. Wang, H.; Shu, Y. Y.; Zheng, M. Y.; Zhang, T., Selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde over SiO(2) supported nickel phosphide catalysts. *Catalysis Letters* **2008**, 124 (3-4), 219-225.
26. Rensel, D. J.; Rouvimov, S.; Gin, M. E.; Hicks, J. C., Highly selective bimetallic FeMoP catalyst for C-O bond cleavage of aryl ethers. *J. Catal.* **2013**, 305, 256-263.
27. Rensel, D. J.; Kim, J.; Jain, V.; Bonita, Y.; Rai, N.; Hicks, J. C., Composition-directed Fe_xMo_{2-x}P bimetallic catalysts for hydrodeoxygenation reactions. *Catal. Sci. Technol.* **2017**, 7, 1857-1867.
28. Bonita, Y.; Hicks, J. C., Periodic trends from metal substitution in bimetallic Mo-based phosphides for hydrodeoxygenation and hydrogenation reactions. *J. Phys. Chem. C* **2018**, 122 (25), 13322-13332.
29. Jain, V.; Bonita, Y.; Brown, A.; Taconi, A.; Hicks, J. C.; Rai, N., Mechanistic insights into hydrodeoxygenation of phenol on bimetallic phosphide catalysts. *Catal. Sci. Technol.* **2018**, 8 (16), 4083-4096.
30. Bonita, Y.; Jain, V.; Geng, F.; O'Connell, T. P.; Wilson, W. N.; Rai, N.; Hicks, J. C., Direct synthesis of furfuryl alcohol from furfural: catalytic performance of monometallic and bimetallic Mo and Ru phosphides. *Catalysis Science & Technology* **2019**.
31. Tan, Q. H.; Wang, G. H.; Long, A.; Dinse, A.; Buda, C.; Shabaker, J.; Resasco, D. E., Mechanistic analysis of the role of metal oxophilicity in the hydrodeoxygenation of anisole. *J. Catal.* **2017**, 347, 102-115.

32. Robinson, A.; Ferguson, G. A.; Gallagher, J. R.; Cheah, S.; Beckham, G. T.; Schaidle, J. A.; Hensley, J. E.; Medlin, J. W., Enhanced hydrodeoxygenation of m-cresol over bimetallic Pt-Mo catalysts through an oxophilic metal-induced tautomerization pathway. *ACS Catal.* **2016**, 6 (7), 4356-4368.
33. Lup, A. N. K.; Abnisa, F.; Daud, W. M. A. W.; Aroua, M. K., Acidity, oxophilicity and hydrogen sticking probability of supported metal catalysts for hydrodeoxygenation process. *IOP Conference Series: Materials Science and Engineering* **2018**, 334, 012074.
34. Hsu, P.-J.; Jiang, J.-W.; Lin, Y.-C., Does a strong oxophilic promoter enhance direct deoxygenation? A study of NiFe, NiMo, and NiW catalysts in p-cresol conversion. *ACS Sustain. Chem. Eng.* **2018**, 6 (1), 660-667.
35. Teles, C. A.; de Souza, P. M.; Braga, A. H.; Rabelo-Neto, R. C.; Teran, A.; Jacobs, G.; Resasco, D. E.; Noronha, F. B., The role of defect sites and oxophilicity of the support on the phenol hydrodeoxygenation reaction. *Applied Catalysis B: Environmental* **2019**, 249, 292-305.
36. Parr, R. G. In *Density functional theory of atoms and molecules*, Horizons of Quantum Chemistry, Dordrecht, 1980//; Fukui, K.; Pullman, B., Eds. Springer Netherlands: Dordrecht, 1980; pp 5-15.
37. Becke, A. D., Perspective: Fifty years of density-functional theory in chemical physics. *J. Chem. Phys.* **2014**, 140 (18).
38. Kresse, G.; Hafner, J., Abinitio molecular-dynamics for liquid-metals. *Phys. Rev. B* **1993**, 47 (1), 558-561.
39. Kresse, G.; Hafner, J., Norm-conserving and ultrasoft pseudopotentials for first-row and transition elements. *J. Phys. Condens. Matter* **1994**, 6 (40), 8245-8257.
40. Kresse, G.; Hafner, J., Ab-Initio molecular-dynamics simulation of the liquid-metal amorphous-semiconductor transition in germanium. *Phys. Rev. B* **1994**, 49 (20), 14251-14269.
41. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, 54 (16), 11169-11186.
42. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.* **1996**, 6 (1), 15-50.

43. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, 59 (3), 1758-1775.
44. Klimeš, J.; Bowler, D. R.; Michaelides, A., Chemical accuracy for the van der Waals density functional. *J. Phys. Condens. Matter* **2009**, 22 (2), 022201.
45. Klimeš, J.; Bowler, D. R.; Michaelides, A., Van der Waals density functionals applied to solids. *Phys. Rev. B* **2011**, 83 (19).
46. Blöchl, P. E., Projector augmented-wave method. *Phys. Rev. B* **1994**, 50 (24), 17953-17979.
47. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab-Initio calculation of vibrational absorption and circular-dichroism spectra using density-functional force-fields. *J. Phys. Chem.* **1994**, 98 (45), 11623-11627.
48. Genova, A.; Pavanello, M., Exploiting the locality of periodic subsystem density-functional theory: efficient sampling of the Brillouin zone. *J. Phys. Condens. Matter* **2015**, 27 (49).
49. Methfessel, M.; Paxton, A. T., High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* **1989**, 40 (6), 3616-3621.
50. Henkelman, G.; Jónsson, H., A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives. *The Journal of Chemical Physics* **1999**, 111 (15), 7010-7022.
51. Ponec, V. On the role of promoters in hydrogenations on metals; α,β -unsaturated aldehydes and ketones. *Appl. Catal. A.* **1997**, 149 (1), 27.
52. Henkelman, G.; Jónsson, H., Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *The Journal of Chemical Physics* **2000**, 113 (22), 9978-9985.
53. Henkelman, G.; Uberuaga, B. P.; Jónsson, H., A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics* **2000**, 113 (22), 9901-9904.
54. Wang, X. Q.; Clark, P.; Oyama, S. T., Synthesis, characterization, and hydrotreating activity of several iron group transition metal phosphides. *J. Catal.* **2002**, 208 (2), 321-331.
55. Oyama, S. T.; Wang, X.; Lee, Y. K.; Bando, K.; Requejo, F. G., Effect of phosphorus content in nickel phosphide catalysts studied by XAFS and other techniques. *J. Catal.* **2002**, 210 (1), 207-217.

56. Wang, A.; Ruan, L.; Teng, Y.; Li, X.; Lu, M.; Ren, J.; Wang, Y.; Hu, Y., Hydrodesulfurization of dibenzothiophene over siliceous MCM-41-supported nickel phosphide catalysts. *J. Catal.* **2005**, 229 (2), 314-321.
57. Wang, L.; Weng, Y.; Wang, X.; Yin, H.; Wang, F.; Xue, X.; Liu, X.; Wang, F.; Duan, P.; Zhang, Y., Synergistic bimetallic RuMo catalysts for selective rearrangement of furfural to cyclopentanol in aqueous phase. *Catal. Commun.* **2019**, 105745.
58. Tamura, M.; Yuasa, N.; Nakagawa, Y.; Tomishige, K., Selective hydrogenation of nitroarenes to aminoarenes using a MoO_x-modified Ru/SiO₂ catalyst under mild conditions. *Chem. Commun.* **2017**, 53 (23), 3377-3380.
59. Chen, L.; Zhu, Y.; Zheng, H.; Zhang, C.; Zhang, B.; Li, Y., Aqueous-phase hydrodeoxygenation of carboxylic acids to alcohols or alkanes over supported Ru catalysts. *Journal of Molecular Catalysis A: Chemical* **2011**, 351, 217-227.
60. Hengne, A. M.; Biradar, N. S.; Rode, C. V., Surface species of supported ruthenium catalysts in selective hydrogenation of levulinic esters for bio-refinery application. *Catal. Lett.* **2012**, 142 (6), 779-787.
61. Clark, P. A.; Oyama, S. T., Alumina-supported molybdenum phosphide hydroprocessing catalysts. *J. Catal.* **2003**, 218 (1), 78-87.
62. Cheng, R.; Shu, Y.; Li, L.; Zheng, M.; Wang, X.; Wang, A.; Zhang, T., Synthesis and characterization of high surface area molybdenum phosphide. *Applied Catalysis A: General* **2007**, 316 (2), 160-168.
63. Basila, M. R.; Kantner, T. R.; Rhee, K. H., The nature of the acidic sites on a silica-alumina. Characterization by infrared spectroscopic studies of trimethylamine and pyridine chemisorption. *J. Phys. Chem.* **1964**, 68 (11), 3197-3207.
64. Zaki, M. I.; Hasan, M. A.; Al-Sagheer, F. A.; Pasupulety, L., In situ FTIR spectra of pyridine adsorbed on SiO₂-Al₂O₃, TiO₂, ZrO₂ and CeO₂: general considerations for the identification of acid sites on surfaces of finely divided metal oxides. *Colloid Surf., A* **2001**, 190 (3), 261-274.
65. Lee, Y. K.; Oyama, S. T., Bifunctional nature of a SiO₂-supported Ni₂P catalyst for hydrotreating: EXAFS and FTIR studies. *J. Catal.* **2006**, 239 (2), 376-389.
66. Bonita, Y.; O'Connell, T. P.; Miller, H. E.; Hicks, J. C., Revealing the hydrogenation performance of RuMo phosphide for chemoselective

reduction of functionalized aromatic hydrocarbons. *Industrial & Engineering Chemistry Research* **2019**, 58 (9), 3650-3658.

67. Neri, G.; Bonaccorsi, L.; Galvagno, S., Kinetic analysis of cinnamaldehyde hydrogenation over alumina-supported ruthenium catalysts. *Ind. Eng. Chem. Res.* **1997**, 36 (9), 3554-3562.
68. Xu, J.; Liu, T.; Li, J.; Li, B.; Liu, Y.; Zhang, B.; Xiong, D.; Amorim, I.; Li, W.; Liu, L., Boosting the hydrogen evolution performance of ruthenium clusters through synergistic coupling with cobalt phosphide. *Energ Environ Sci* **2018**, 11 (7), 1819-1827.
69. Chen, J. X.; Yang, Y.; Shi, H.; Li, M. F.; Chu, Y.; Pan, Z. Y.; Yu, X. B., Regulating product distribution in deoxygenation of methyl laurate on silica-supported Ni-Mo phosphides: Effect of Ni/Mo ratio. *Fuel* **2014**, 129, 1-10.
70. Rodriguez, J. A.; Kim, J. Y.; Hanson, J. C.; Sawhill, S. J.; Bussell, M. E., Physical and chemical properties of MoP, Ni₂P, and MoNiP hydrodesulfurization catalysts: Time-resolved X-ray diffraction, density functional, and hydrodesulfurization activity studies. *J. Phys. Chem. B* **2003**, 107 (26), 6276-6285.
71. Schoenbaum, C. A.; Schwartz, D. K.; Medlin, J. W., Controlling the Surface Environment of Heterogeneous Catalysts Using Self-Assembled Monolayers. *Accounts Chem Res* **2014**, 47 (4), 1438-1445.
72. Gao, R.; Pan, L.; Wang, H.; Yao, Y.; Zhang, X.; Wang, L.; Zou, J.-J., Breaking trade-off between selectivity and activity of nickel-based hydrogenation catalysts by tuning both steric effect and d-band center. *Advanced Science* **2019**, 6 (10), 1900054.
73. Li, Y.; Cheng, H.; Lin, W.; Zhang, C.; Wu, Q.; Zhao, F.; Arai, M., Solvent effects on heterogeneous catalysis in the selective hydrogenation of cinnamaldehyde over a conventional Pd/C catalyst. *Catalysis Science & Technology* **2018**, 8 (14), 3580-3589.
74. Lan, X.; Xue, K.; Wang, T., Combined synergetic and steric effects for highly selective hydrogenation of unsaturated aldehyde. *J. Catal.* **2019**, 372, 49-60.
75. Ponec, V., On the role of promoters in hydrogenations on metals; α,β -unsaturated aldehydes and ketones. *Applied Catalysis A: General* **1997**, 149 (1), 27-48.

76. Avery, N. R.; Weinberg, W. H.; Anton, A. B.; Toby, B. H., End-On and Side-On Bonding of Ketones to Surfaces: Acetone on the Ru(001) and Pt(111) Surfaces. *Phys Rev Lett* **1983**, *51* (8), 682-685.
77. Srivastava, R. D.; Guha, A. K., Kinetics and mechanism of deactivation of Pd/Al₂O₃ catalyst in the gaseous phase decarbonylation of furfural. *J. Catal.* **1985**, *91* (2), 254-262.
78. Nishiyama, S.; Hara, T.; Tsuruya, S.; Masai, M., Infrared Spectroscopy Study of Aldehydes Adsorbed on Rh–Sn Bimetallic Systems: Selective Activation of Aldehydes by Tin. *The Journal of Physical Chemistry B* **1999**, *103* (21), 4431-4439.
79. Delbecq, F.; Sautet, P., Competitive C • C and C • O Adsorption of α - β -Unsaturated Aldehydes on Pt and Pd Surfaces in Relation with the Selectivity of Hydrogenation Reactions: A Theoretical Approach. *J. Catal.* **1995**, *152* (2), 217-236.

CHAPTER 7

SUMMARY AND FUTURE WORKS

7.1 Chapter overview

The encompassing theme of this thesis is to gain deeper understanding of bimetallic phosphide catalysts for the upgrading of complex biomass feed as detailed in the Chapter 1. Therefore, this goal was accomplished by synthesizing various bimetallic phosphides and their respective monometallic phosphides, subject them to various characterization techniques, and evaluating selected materials for reactions that are of importance in biomass upgrading (Chapter 1).¹⁻

⁴ Additionally, supporting computational calculation through collaboration with other research group was also utilized to complement the experimental work. This Chapter attempts to summarize the research efforts and findings in this thesis and discusses future work on this subject.

7.2 Periodic trends from metal substitution in bimetallic Mo-based phosphides for hydrodeoxygenation and hydrogenation reactions

In Chapter 3, a variety of period 4 and 5 unsupported Mo-based bimetallic phosphides ($M\text{MoP}$, $M = \text{Fe, Co, Ni, Ru}$) were synthesized with the TPR method.

The bulk and surface oxidation state of the materials were thoroughly examined with XANES and XPS respectively. The results show the charge sharing between the metals and phosphorus control the relative oxidation of Mo and reduction of P in the lattice, which were both indirectly observed in binding energy shifts in XPS and absorption energy shifts in XANES. For *MMoP* (*M*= Fe, Co, Ni), the more oxidized the Mo in the bimetallic phosphide, the higher the selectivity to benzene from phenol via direct deoxygenation at 400°C and 750 psig. This phenomenon was observed in the bimetallic materials synthesized across period 4, where aromatic selectivity and degree of Mo oxidation both decreased in the following order FeMoP >> CoMoP > NiMoP. Alternatively, in the case of *MMoP* (*M* = Fe, Ru), the P in RuMoP is more oxidized compared to FeMoP and, the selectivity towards the hydrogenation pathway increased due to the interaction between the aromatic rings and the P species on the surface.

For RuMoP and NiMoP, cyclohexanol was selectively produced from phenol with >99% selectivity when the reaction temperature was lowered to 125°C at 750 psig, whereas FeMoP and CoMoP were not active under these conditions. Lastly, complete deoxygenation of phenol to benzene, cyclohexane and cyclohexene was accomplished using mixtures of RuMoP and FeMoP in flow and batch experiments. These results highlight the versatility and wide applicability of transition metal phosphides for biomass conversions.

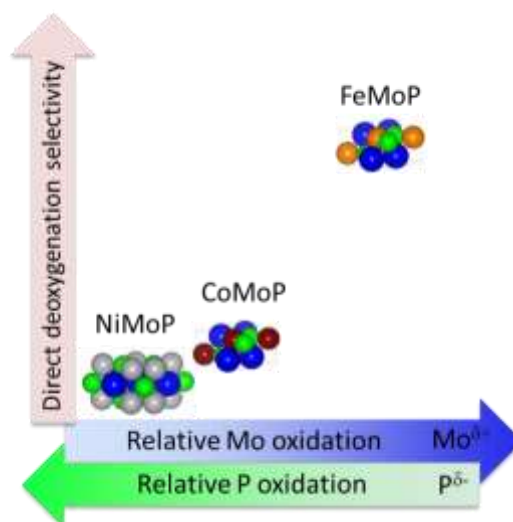


Figure 7.1. Correlation between relative oxidation of Mo and P with the direct deoxygenation selectivity in phenol HDO.

7.3 Revealing the hydrogenation performance of RuMo phosphides for chemoselective reduction of functionalized aromatic hydrocarbons

Chapter 4 explores further the chemoselective hydrogenation ability of RuMoP using various functionalized aromatic hydrocarbons to provide insight into how the functional groups compete for reduction on the surface of RuMoP. This work is motivated by the low temperature results in Chapter 3. High selectivity (~99%) to reduction of the substituent is achieved for the hydrogenation of electron withdrawing functionalities such as nitrobenzene, benzaldehyde, and benzophenone with RuMoP to yield aniline, benzyl alcohol, and diphenylmethanol, respectively. In contrast, aromatics with electron donating groups such as phenol, anisole, and toluene, show high ring hydrogenation selectivity (~99%) to form cyclohexanol, methoxycyclohexane, and methyl cyclohexane, respectively, although the reaction proceeded slowly with RuMoP.

Pyridine adsorption was studied via diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), which provided evidence of surface electron deficient sites (i.e., Lewis acids) that are responsible for targeting the electron rich portion of the substrate. Additional DRIFTS experiments were performed using nitrobenzene, anisole, and a mixture of the two. From these experiments, features associated with -NO_2 adsorption in nitrobenzene and ring adsorption in anisole were observed, which correlated well with the observed reaction results. Finally, a solvent study provided evidence for the competitive adsorption of the lone pair of isopropanol and the π -electrons from the aromatic ring of phenol with the former being more favorable on RuMoP surface.

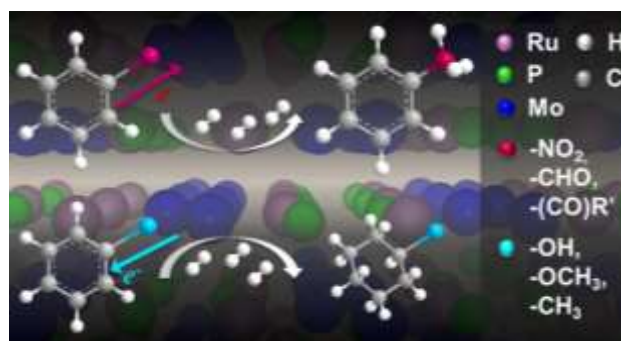


Figure 7.2. Hydrogenation of functionalized aromatics with electron withdrawing group and electron donating group using RuMoP.

7.4 Direct synthesis of furfuryl alcohol from furfural: Catalytic performance of monometallic and bimetallic Mo and Ru phosphides

In Chapter 4, the catalytic properties of monometallic and bimetallic Ru and Mo phosphides were evaluated for their ability to selectively hydrogenate furfural to furfuryl alcohol. Monometallic MoP showed high selectivity (98%)

towards furfuryl alcohol, while RuP and Ru₂P exhibited lower selectivity at comparable conversion. Bimetallic promotional effects were observed with Ru_{1.0}Mo_{1.0}P, as the pseudo-first order reaction rate constant for furfural hydrogenation to furfuryl alcohol, k_1 , was at least 5x higher than MoP, RuP, and Ru₂P, while maintaining a 99% selectivity. Composition-directed catalytic studies of Ru_xMo_{2-x}P ($0.8 < x < 1.2$) provided evidence that Ru rich compositions positively influence k_1 , but not the selectivity. The rate constant ratio (k_1/k_2+k_3) for furfuryl alcohol production compared to methyl furan (k_2) and tetrahydrofurfuryl alcohol (k_3) followed the trend of Ru_{1.0}Mo_{1.0}P > Ru_{1.2}Mo_{0.8}P > MoP > Ru_{0.8}Mo_{1.2}P > RuP > Ru₂P. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to examine the configuration of adsorbed furfural on the synthesized catalysts, but the results were inconclusive and no correlation could be found with the selectivity due to the IR inactive surface modes possible with furfural adsorption. However, gas phase density functional theory calculations suggested the $x = 1$ material in Ru_xMo_{2-x}P ($0.8 < x < 1.2$) had the most favorable furfural adsorption energy. Experimentally, we also observed that the solvent greatly influenced both the conversion and selectivity, where isopropanol provided the highest selectivities to furfuryl alcohol. Finally, recycling experiments showed a 12% decrease in k_1 after 3 cycles without any regeneration, but the activity could be fully recovered through a re-reduction step.

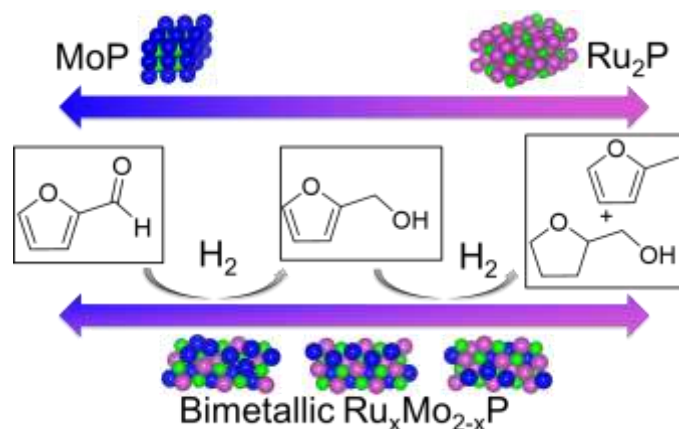


Figure 7.3. Furfural hydrogenation reaction with various composition of $\text{Ru}_x\text{Mo}_{2-x}\text{P}$.

7.5 Hydrogenation of cinnamaldehyde with bimetallic phosphides: Effect of metal composition and observation of product-induced reaction modulation

Selective hydrogenation of α,β -unsaturated aldehydes is challenging due to the competition between unsaturated moieties ($\text{C}=\text{C}$ and $\text{C}=\text{O}$) on the catalyst surface. This study probes the use of metal phosphides (monometallic and bimetallic compositions) as selective catalysts for cinnamaldehyde hydrogenation. Monometallic phosphides MP ($\text{M} = \text{Ni}, \text{Co}, \text{Ru}$) showed high affinity to $\text{C}=\text{C}$ bond hydrogenation, with 98% selectivity to hydrocinnamaldehyde (HCAL) with both Ni_2P and Co_2P . In contrast, monometallic MoP favored $\text{C}=\text{O}$ reduction with a 77% selectivity to cinnamyl alcohol (COL). Ru addition to Mo phosphide to form bimetallic RuMoP improved the COL selectivity up to 91%, while Ni addition to Mo form bimetallic NiMoP preferred the $\text{C}=\text{C}$ hydrogenation to HCAL. Density functional theory (DFT) suggested that the Lewis acid character (i.e., $\text{Mo}^{\delta+}$) was enhanced with Ru due to charge transfers between the

metals and P atom. Modulation studies showed that the C=O hydrogenation products (both saturated and unsaturated) created surface steric effects that aid adsorption through C=O and increase the selectivity to COL. Furthermore, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy studies of CAL adsorption showed the $\eta_1(\text{O})$ adsorption mode in RuMoP that accounts for COL formation, while an additional C=O feature on NiMoP possibly due to π -bonded C=O or 1,4-diadsorbed species inhibited COL formation. Lastly, DFT calculations suggested that H₂ addition is more favorable across C=O for RuMoP and C=C for NiMoP, which confirmed the experimental results.

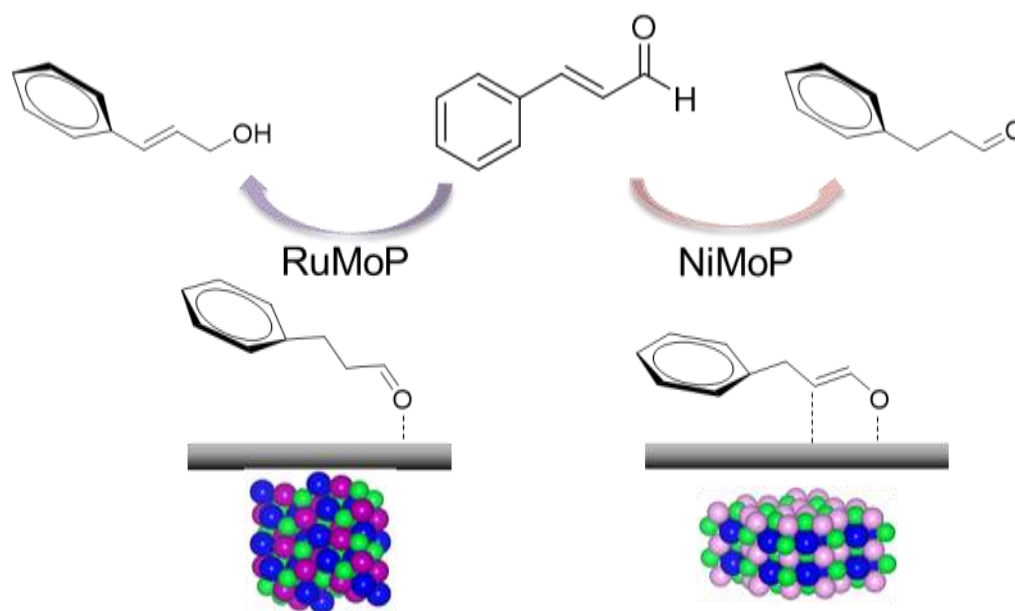


Figure 7.4. Hydrogenation of cinnamaldehyde to cinnamyl alcohol with RuMoP and to hydrocinnamaldehyde with NiMoP.

7.6 Future work

In Chapter 3 and Chapter 5, surface of bimetallic phosphides can be altered with either metal substitution or changes in composition. This surface electronics heavily influences the catalytic performance of the material. In Chapter 4, 5, and 6, the catalytic properties of RuMoP is thoroughly studied to show promise for lower temperature chemoselective hydrogenation catalyst. However, the studies in Chapter 3-6 only encompasses several bimetallic phosphides metal combinations.

It was briefly mentioned in Chapter 1, there exists a naturally-occurring phosphide catalysts comprising of a variety of Fe-Ni phosphides. The elemental composition of these phosphides is summarized in Figure 7.1 for materials found in meteors (blue) and terrestrially (red). According to the diagram, the Fe-Ni phosphides exists as $\text{Fe}_x\text{Ni}_{3-x}\text{P}$, $\text{Fe}_x\text{Ni}_{2-x}\text{P}$, and $\text{Fe}_x\text{Ni}_{1-x}\text{P}$. Some of these compositions such as monometallic Fe_2P and Ni_2P have been studied for hydrodeoxygenation and hydrogenation reactions.⁵⁻⁶ In fact, Ni_2P (synthesized with various methods) is the most studied phosphide catalyst due to its synthetic favorability and its high activity. However, in most studies and in Chapter 6, Ni_2P is not very selective in heteroatom interactions evident by the higher selectivity in hydrogenation products.⁷ On the other hand, Fe_2P have shown higher deoxygenation selectivity, yet the activity is lower than Ni_2P .⁵ Although some bimetallic Fe-Ni-P studies exist, most of these studies do not explore the naturally occurring Fe-Ni-P ratio.⁸

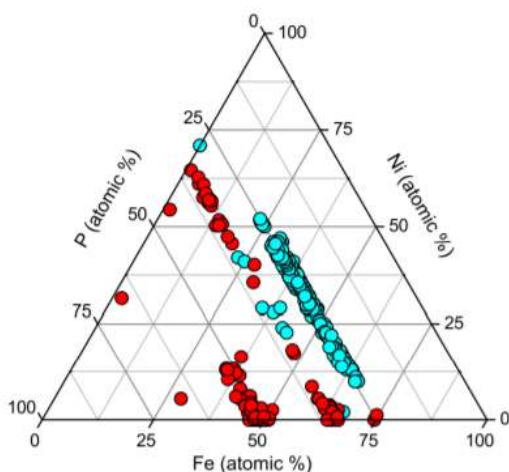


Figure 7.5. Composition of naturally occurring phosphides found in meteorites (blue) and terrestrially (red).⁹

FeNi phosphides supported SiO_2 have been shown as an active and selective catalyst for hydrodesulfurization (HDS) reactions. One of the advantages of studying the Fe_2P , Ni_2P , and $\text{Fe}_x\text{Ni}_{2-x}\text{P}$ system is that the crystal structure is consistently hexagonal. A shift in XRD peak can potentially provide information regarding the second metal incorporation. However, this analysis becomes challenging in supported materials due to the small particle size. Therefore, more powerful techniques such as TEM diffraction or EXAFS are needed to confirm the second metal incorporation.

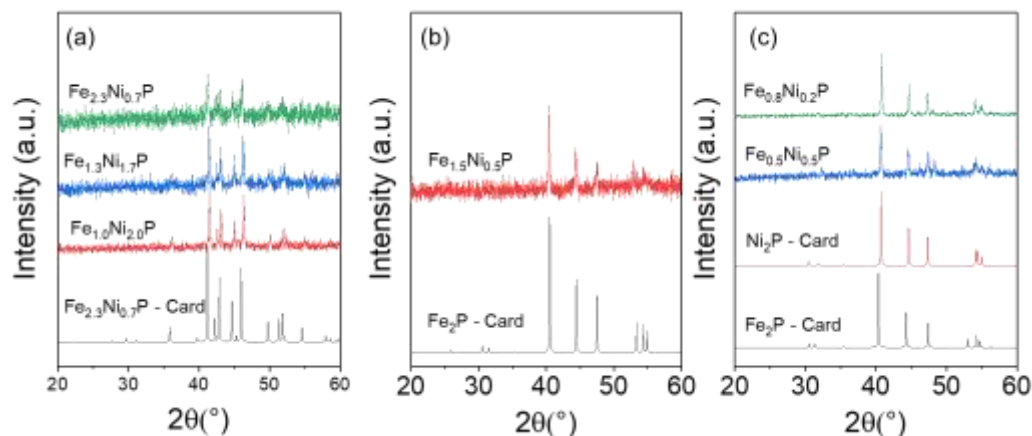


Figure 7.6. XRD of unsupported (a) $\text{Fe}_x\text{Ni}_{3-x}\text{P}$, (b) $\text{Fe}_x\text{Ni}_{2-x}\text{P}$, and (c) $\text{Fe}_x\text{Ni}_{1-x}\text{P}$.

Various unsupported bimetallic $\text{Fe}_x\text{Ni}_{3-x}\text{P}$, $\text{Fe}_x\text{Ni}_{2-x}\text{P}$, and $\text{Fe}_x\text{Ni}_{1-x}\text{P}$ are synthesized according to the TPR method described in Chapter 3-6. The XRD of these materials are presented in Figure 7.6 with their bulk composition determined with ICP-OES. The crystal structure of $\text{Fe}_x\text{Ni}_{3-x}\text{P}$ is orthorhombic, which can be distinguished from the hexagonal monometallic Fe_2P and Ni_2P . Moreover, Fe-rich ($\text{Fe}_{2.24}\text{Ni}_{0.76}\text{P}$) and Ni-rich ($\text{Fe}_{1.0}\text{Ni}_{2.0}\text{P}$) materials can be synthesized with defined crystal structures, aiding the discovery of the optimum composition. In contrast, for the $\text{Fe}_x\text{Ni}_{2-x}\text{P}$ group, only the $\text{Fe}_{1.5}\text{Ni}_{0.5}\text{P}$ can be synthesized with hexagonal crystal structures. Therefore, more synthesis effort to synthesize the other $\text{Fe}_x\text{Ni}_{2-x}\text{P}$ ratio is still needed. Lastly, for the $\text{Fe}_x\text{Ni}_{1-x}\text{P}$ group, impurities at 49° 2θ is observed and the intensity of this impurity increases as the Ni content increases. This impurity comes from the formation of monometallic NiP. Other synthetic parameters such as reduction temperature and time should be explored to remove the impurity peak.

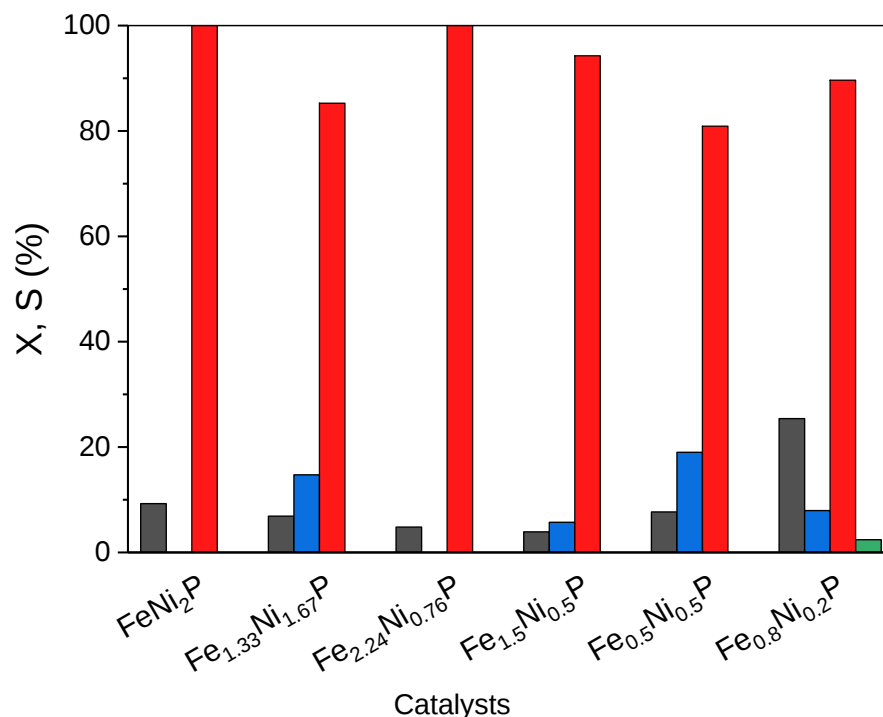


Figure 7.7. Preliminary reaction result for cinnamaldehyde hydrogenation in a batch reactor presented as conversion (X, black) and the selectivity to hydrocinnamaldehyde (S, red), cinnamyl alcohol (S, blue), and benzene propanol (S, green).

The synthesized materials presented in Figure 7.6 was tested for CAL hydrogenation at 125°C and 600 psig H₂ in a batch reactor. All tested materials have high selectivity to the hydrogenation of C=C bond (hydrocinnamaldehyde). For the Fe-rich (Fe_{2.24}Ni_{0.76}P) and Ni-rich (Fe_{1.0}Ni_{2.0}P) materials in Fe_xNi_{3-x}P, the selectivity is >99% to hydrocinnamaldehyde. However, Fe_{1.33}Ni_{1.67}P shows a decrease in hydrocinnamaldehyde selectivity to 85%, while the selectivity to cinnamyl alcohol increases to 15%. In this study, only Fe_{0.5}Ni_{0.5}P has higher selectivity to cinnamyl alcohol to 19%. The preliminary result suggests that cinnamyl alcohol is predominantly produced on materials closer to 1:1 ratio of Fe:Ni. This result agrees with studies in Chapter 3 where better surface charge

transfer is observed on well-distributed atoms, which increases the surface-O interaction on oxygenated substrates.

Despite the preliminary results, the Fe-Ni-P systems are not particularly selective for cinnamaldehyde hydrogenation. Due to the absence of noble metal in the system, low temperature hydrogenation may not be the recommended application of the Fe-Ni-P materials. Moreover, synthetic improvements are still needed to obtain better diffraction patterns free of impurities. Therefore, many research efforts are still needed for this material.

7.7 References

1. Jain, V.; Bonita, Y.; Brown, A.; Taconi, A.; Hicks, J. C.; Rai, N., Mechanistic insights into hydrodeoxygenation of phenol on bimetallic phosphide catalysts. *Catal. Sci. Technol.* **2018**, 8 (16), 4083-4096.
2. Bonita, Y.; Hicks, J. C., Periodic trends from metal substitution in bimetallic Mo-based phosphides for hydrodeoxygenation and hydrogenation reactions. *J. Phys. Chem. C* **2018**, 122 (25), 13322-13332.
3. Bonita, Y.; Hicks, J. C., Metal phosphides and their applications in catalysis. In *Alternative catalytic materials: carbides, nitrides, phosphides, and amorphous boron alloys*, Hargreaves, J. S. J.; McFarlane, A. R.; Kaassiri, S., Eds. Royal Society of Chemistry: Croydon, UK, 2018.
4. Bonita, Y.; Jain, V.; Geng, F.; O'Connell, T. P.; Wilson, W. N.; Rai, N.; Hicks, J. C., Direct synthesis of furfuryl alcohol from furfural: catalytic performance of monometallic and bimetallic Mo and Ru phosphides. *Catal. Sci. Technol.* **2019**, 9 (14), 3656-3668.
5. Rodríguez-Aguado, E.; Infantes-Molina, A.; Ballesteros-Plata, D.; Cecilia, J. A.; Barroso-Martín, I.; Rodríguez-Castellón, E., Ni and Fe mixed phosphides catalysts for O-removal of a bio-oil model molecule from lignocellulosic biomass. *Mol Catal* **2017**, 437, 130-139.
6. Bui, P.; Cecilia, J. A.; Oyama, S. T.; Takagaki, A.; Infantes-Molina, A.; Zhao, H. Y.; Li, D.; Rodriguez-Castellon, E.; Lopez, A. J., Studies of the synthesis of transition metal phosphides and their activity in the

- hydrodeoxygenation of a biofuel model compound. *J. Catal.* **2012**, 294, 184-198.
7. Li, K. L.; Wang, R. J.; Chen, J. X., Hydrodeoxygenation of anisole over silica-supported Ni₂P, MoP, and NiMoP catalysts. *Energ. Fuel* **2011**, 25 (3), 854-863.
 8. Cho, A.; Shin, J.; Takagaki, A.; Kikuchi, R.; Oyama, S. T., Ligand and ensemble effects in bimetallic NiFe phosphide catalysts for the hydrodeoxygenation of 2-methyltetrahydrofuran. *Top. Catal.* **2012**, 55 (14-15), 969-980.
 9. Britvin, S. N.; Murashko, M. N.; Vapnik, Y.; Polekhovsky, Y. S.; Krivovichev, S. V., Earth's Phosphides in Levant and insights into the source of Archean prebiotic phosphorus. *Sci. Rep.* **2015**, 5.

APPENDIX

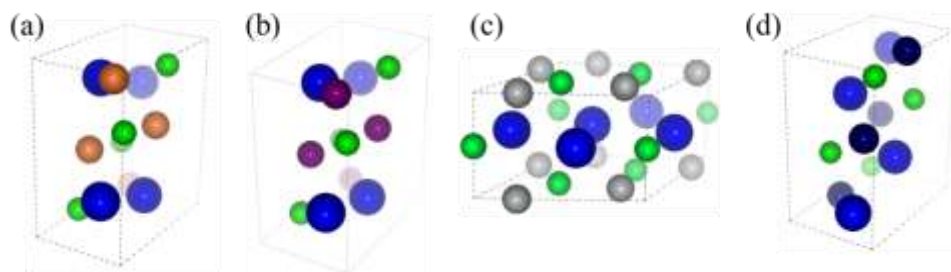


Figure A.1. Unit cell representation of (a) FeMoP (b) CoMoP (c) NiMoP and (d) RuMoP where atoms in blue represents Mo, green is P, orange is Fe, purple is Co, gray is Ni, and black is Ru. VESTA software was used to produce the drawings.

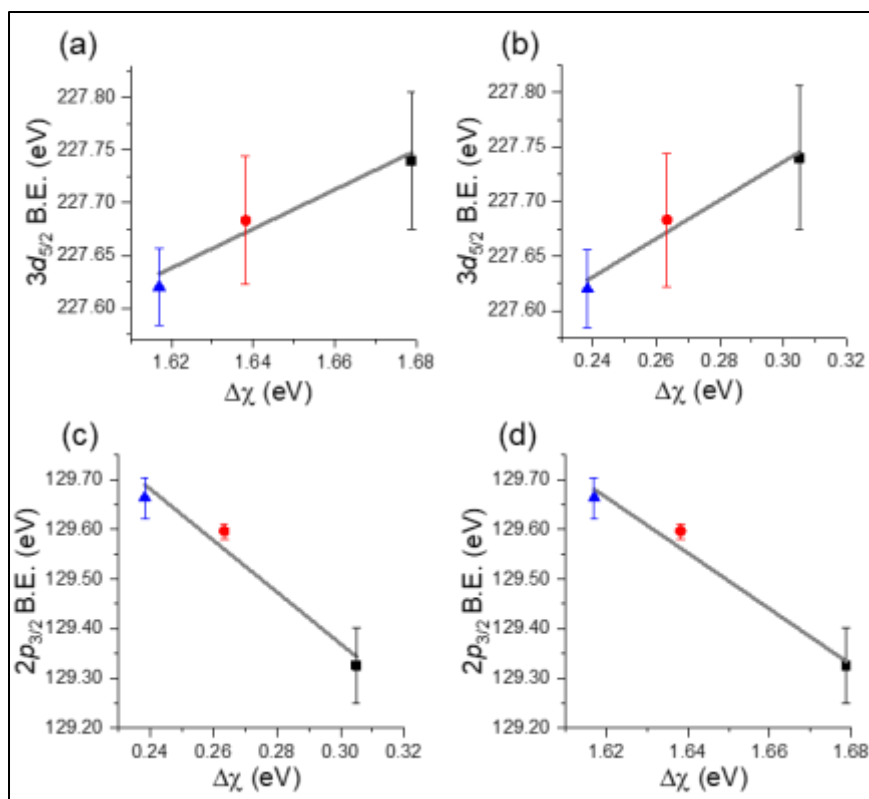


Figure A.2. The relationship between electronegativity difference and binding energy of (a,c) P $2p_{3/2}$ and (b,d) Mo $3d_{5/2}$ for NiMoP (blue triangle), CoMoP (red circle), and FeMoP (black square). Figure (a) and (b) are calculated using Mulliken electronegativity scale. Figure (c) and (d) are calculated using Pauling electronegativity scale.

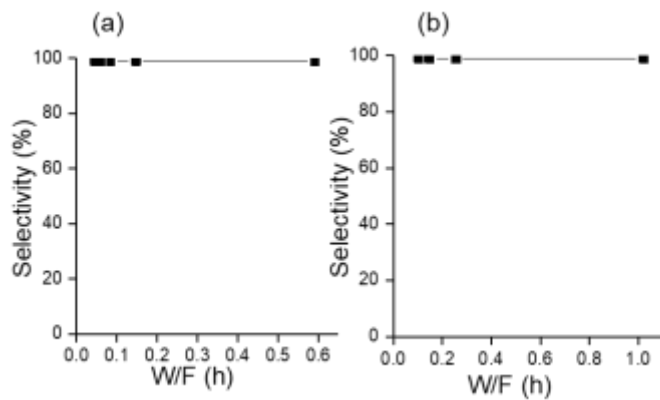


Figure A.3. W/F study of (a) NiMoP and (b) RuMoP for phenol HDO at 125°C and 750 psig.

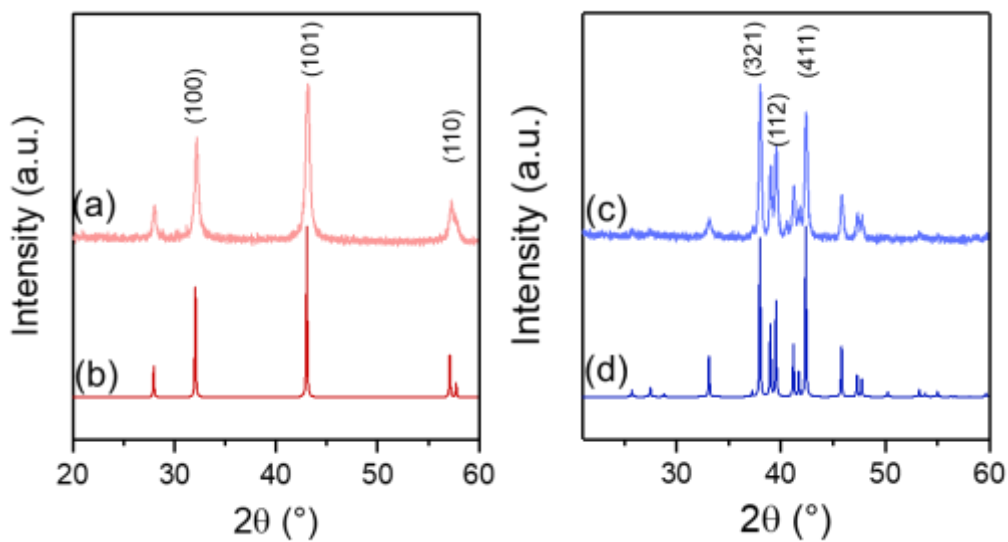


Figure A.4. XRD patterns of (a) MoP (b) MoP reference (PDF 04-002-4743) (c) Mo₃P (d) Mo₃P reference (PDF 03-065-1609).

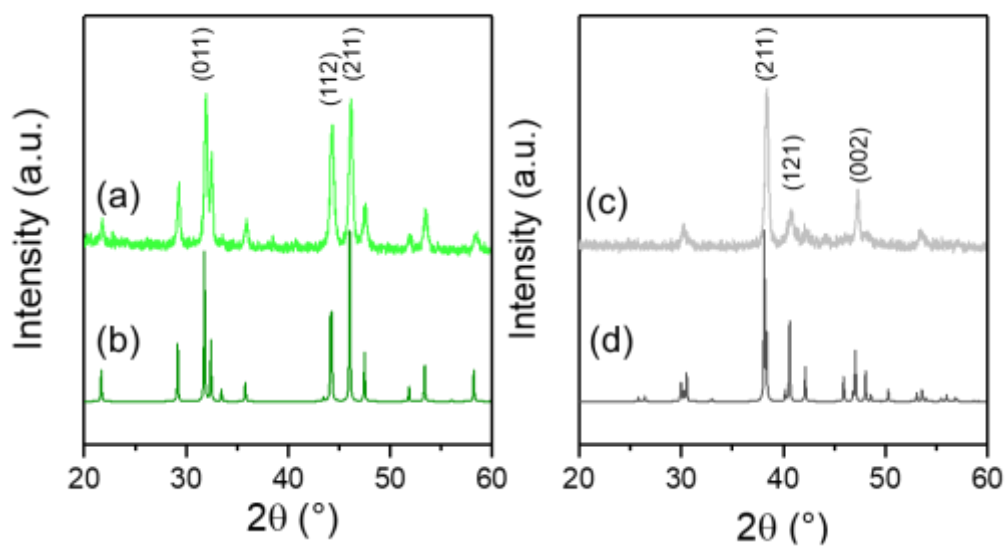


Figure A.5. XRD patterns of (a) RuP (b) RuP reference (PDF 04-004-3077) (c) Ru₂P (d) Ru₂P reference (PDF 04-004-4140).

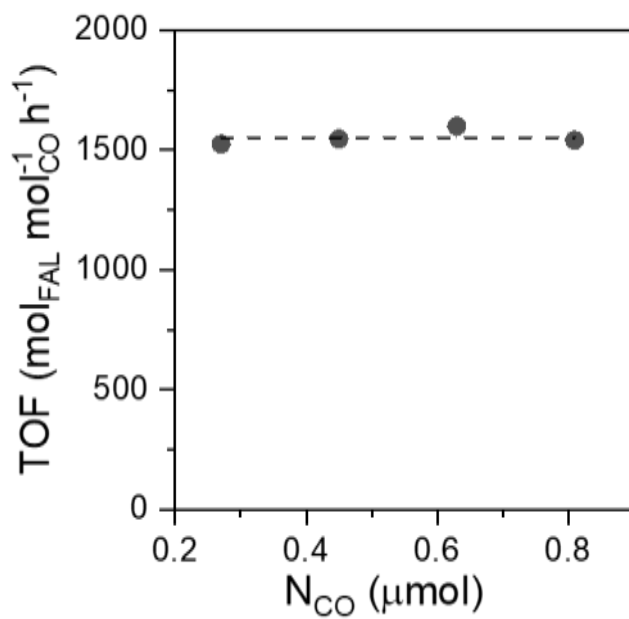


Figure A.6. TOF correlation with the increase in amount of catalyst used in the experiments. The difference between each point are < 5%.

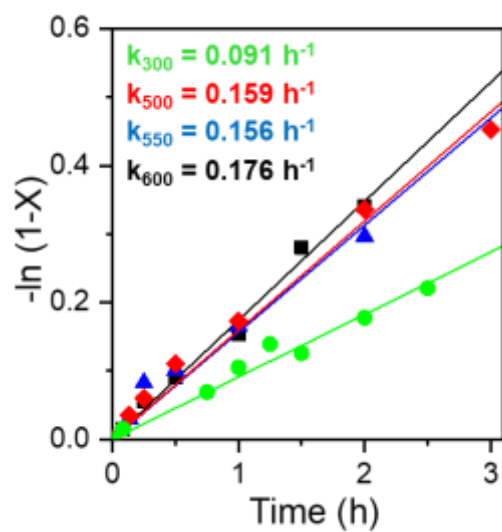


Figure A.7. H_2 dependency for FAL hydrogenation with $\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$ reaction performed at 2.0 MPa (green – $R^2 = 0.973$), 3.4 MPa (red – $R^2 = 0.983$), 3.8 MPa (blue – $R^2 = 0.946$), and 4.2 MPa (black – $R^2 = 0.981$) H_2 partial pressure and total pressure of 4.2 MPa at 100°C and 0.10 M FAL in IPA.

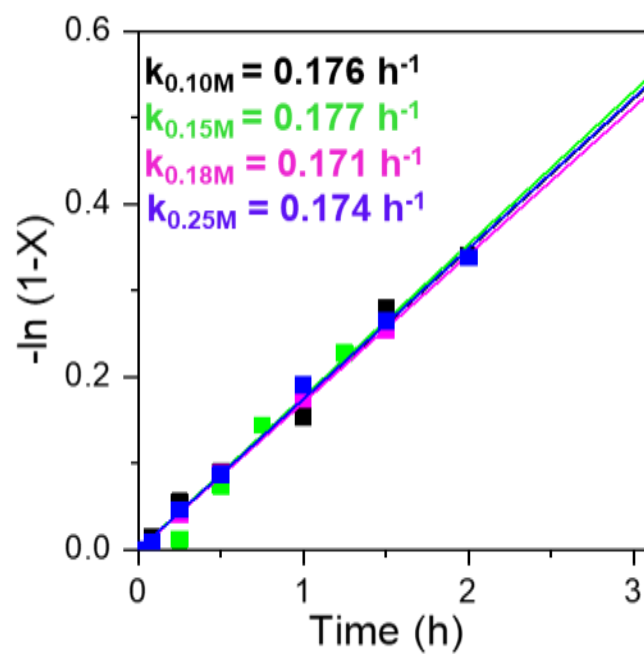


Figure A.8. (a) First order dependency of FAL concentration measured for initial concentration of 0.10 M (black – $R^2 = 0.981$), 0.15 M (green – $R^2 = 0.975$), 0.18 M (magenta – $R^2 = 0.978$), and 0.25 M (blue – $R^2 = 0.986$).

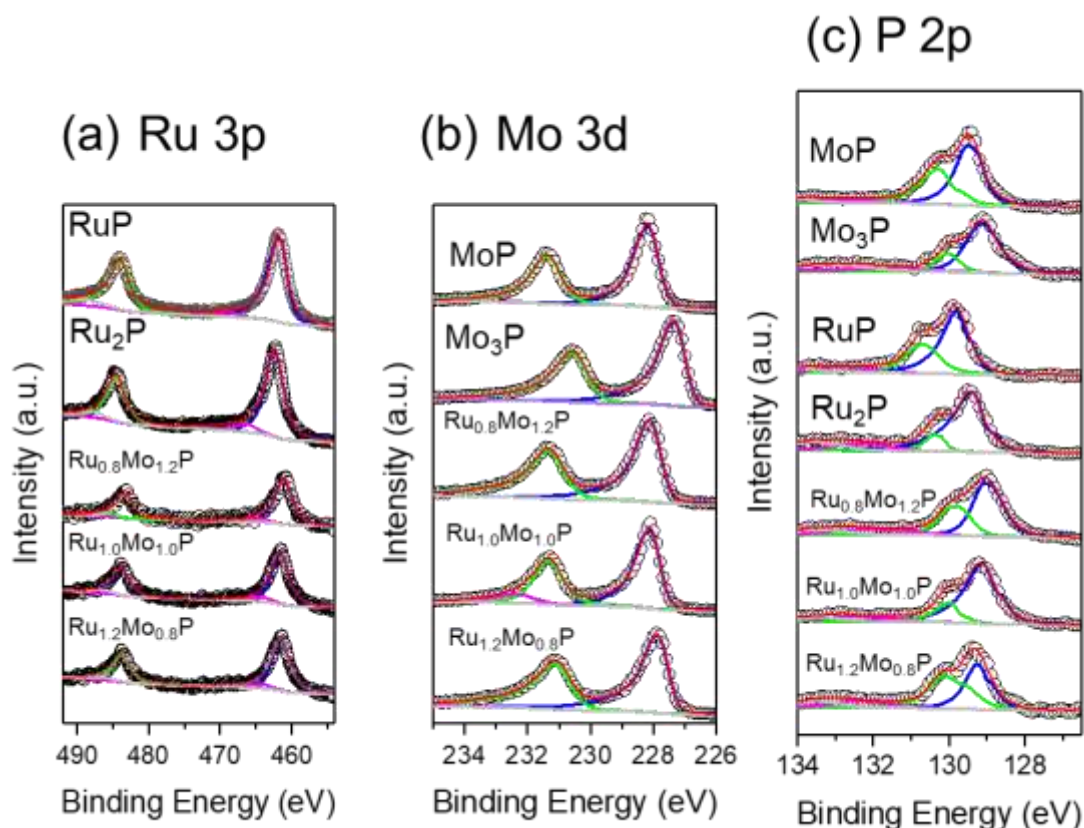


Figure A.9. XP spectra deconvolution for (a) reduced Ru 3p_{3/2} (blue), reduced Ru 3p_{1/2} (green), oxidized Ru 3p_{3/2} (magenta), oxidized Ru 3p_{1/2} (gray), (b) reduced Mo 3d_{5/2} (blue), reduced Mo 3d_{3/2} (green), oxidized Mo 3d_{5/2} (magenta), oxidized Mo 3d_{3/2} (gray), and (c) reduced P 2p_{3/2} (blue), reduced P 2p_{1/2} (green), oxidized P 2p_{3/2} (magenta), oxidized P 2p_{1/2} (gray). The raw spectrum is represented by the empty circles and the fit is represented by the red line.

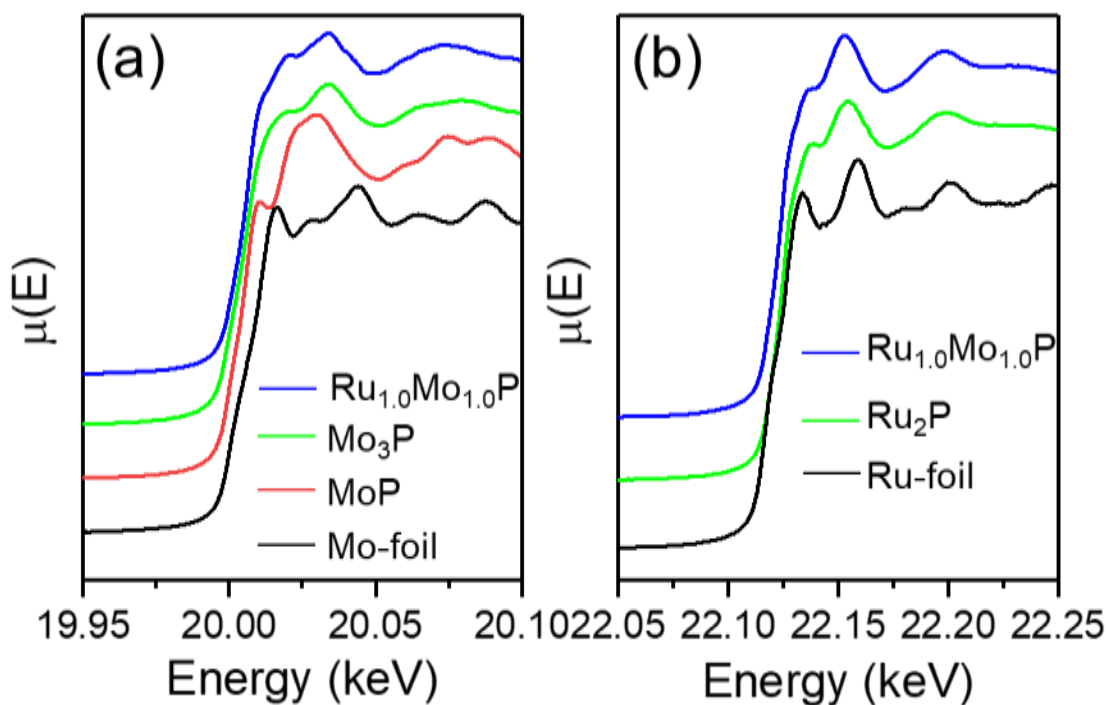


Figure A.10. (a) Mo K-edge XANES spectra of Mo-foil (black), MoP (red), Mo₃P (green), Ru_{1.0}Mo_{1.0}P (blue) and (b) Ru K-edge XANES spectra of Ru-foil (black), Ru₂P (green), Ru_{1.0}Mo_{1.0}P (blue).

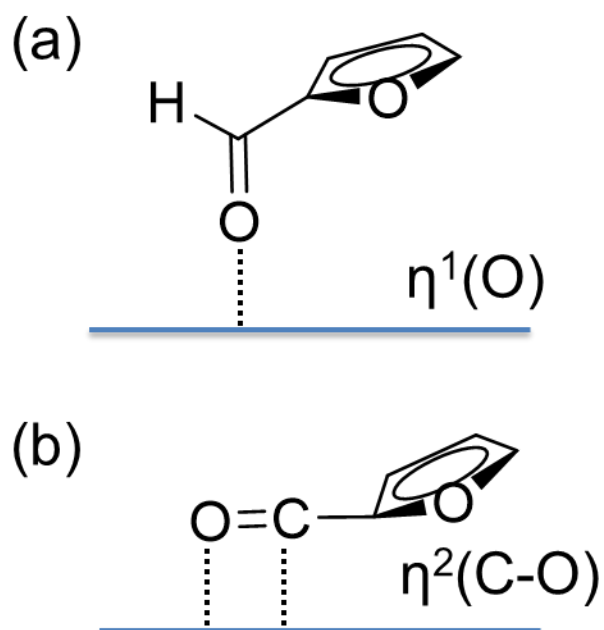


Figure A.11. Two possible adsorption modes on the catalyst surface: (a) $\eta^1(\text{O})$ was observed on Cu, (b) $\eta^2(\text{C-O})$ suggested on group VIII metals.

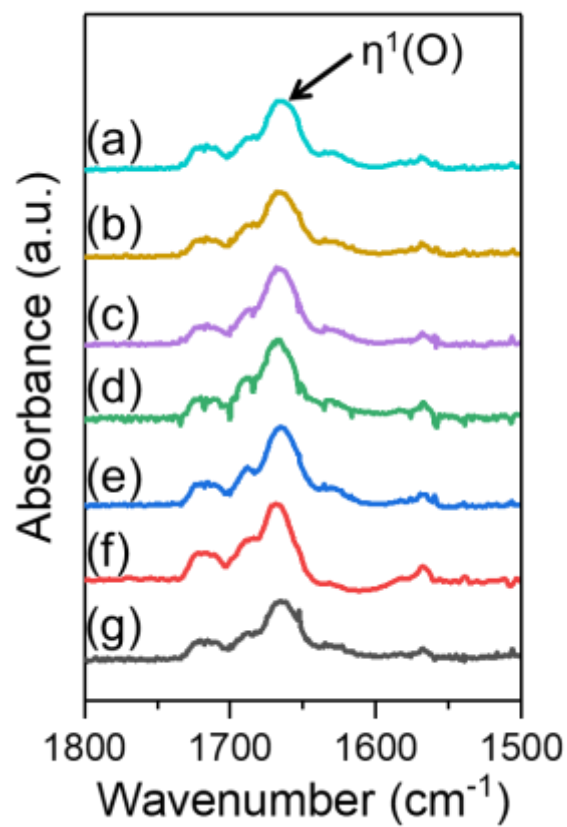


Figure A.12. DRIFT spectra of FAL on (a) Cu/SiO₂ (b) MoP (c) Ru₂P (d) RuP (e) Ru_{0.8}Mo_{1.2}P (f) Ru_{1.0}Mo_{1.0}P (g) Ru_{0.8}Mo_{1.2}P.

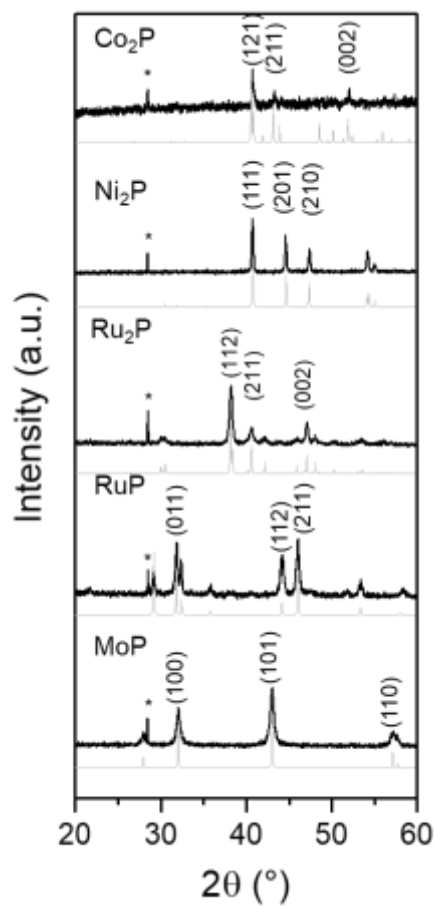


Figure A.13. X-ray diffraction pattern of monometallic phosphides (black) Co_2P , Ni_2P , Ru_2P , RuP , MoP and their respective reference patterns (gray). All peaks are shifted with respect to Si(111) peak at 28.44° marked with star (*).

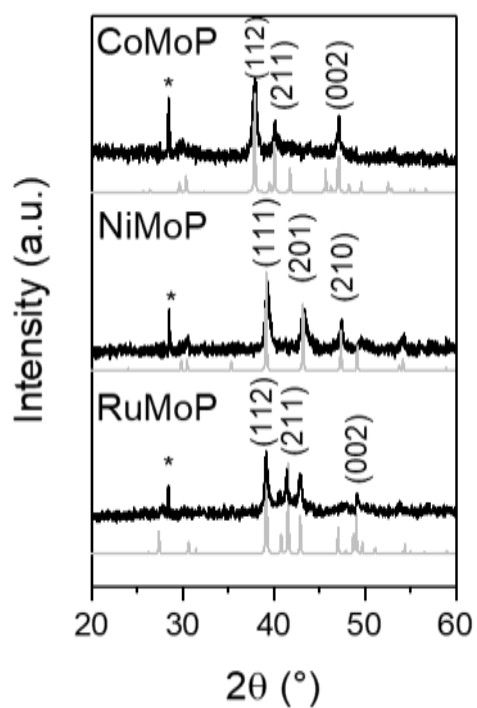


Figure A.14. X-ray diffraction pattern of bimetallic phosphides (black) CoMoP, NiMoP, and RuMoP and their respective reference patterns (gray). All peaks are shifted with respect to Si(111) peak at 28.44° marked with star (*).

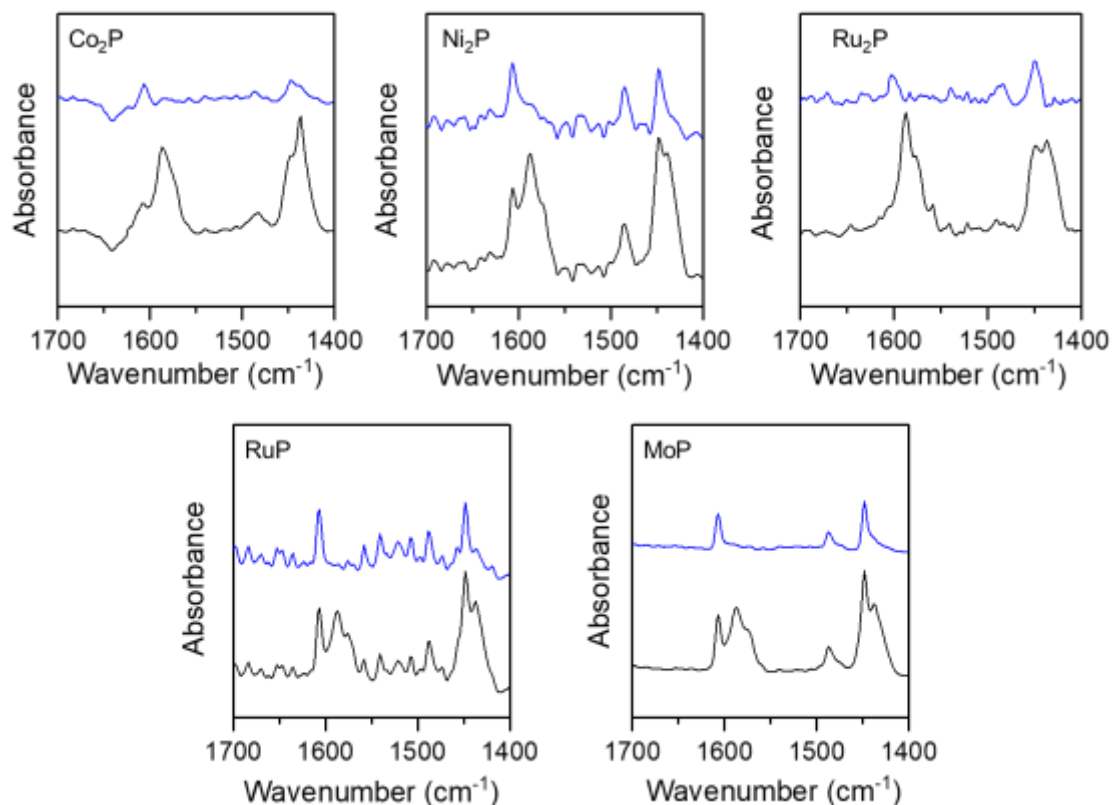


Figure A.15. Pyridine adsorption observed under DRIFT spectroscopy for Co_2P , Ni_2P , Ru_2P , RuP , and MoP during pyridine saturation (black) and after N_2 purging (blue) at 50°C .

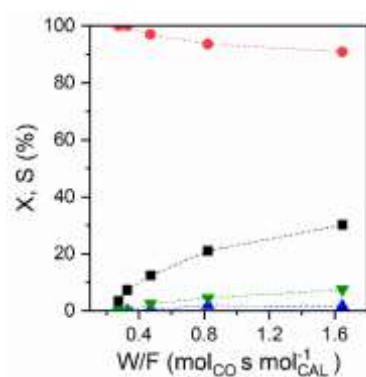


Figure A.16. Conversion (X – black) and selectivity (S) of COL(blue), HCAL (red), and HCOL (green) as a function of W/F for (a) NiMoP and (b) RuMoP .

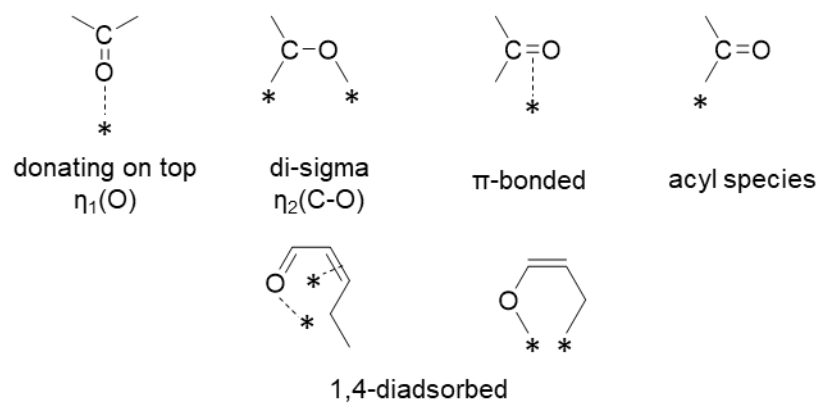


Figure A.17. Possible C=O adsorption on catalyst surface.

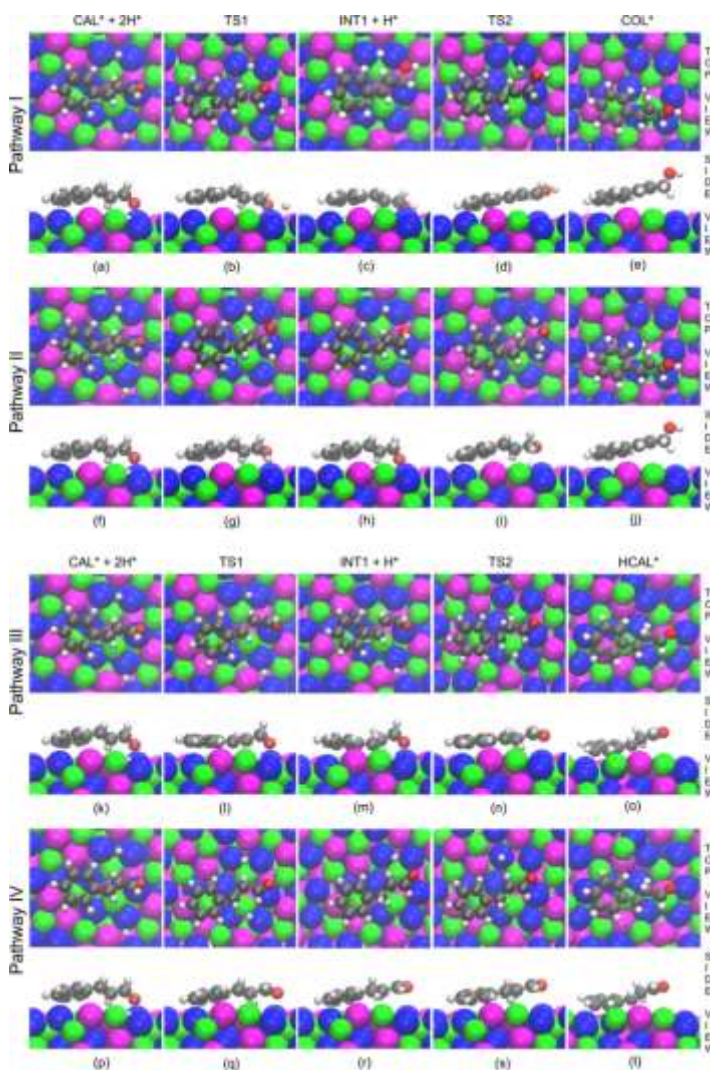


Figure A.18. Optimized structures of CAL, COL, HCAL, and reaction intermediates on the (112) facet of RuMoP during COL and HCAL reaction pathway (via pathway I, II, III & IV): (a), (f), (k) & (p) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CHO}^*$ and 2H^* , (b) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CHO-H}^*$ (TS1; pathway I) and H^* , (g) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{C-HHO}^*$ (TS1; pathway II) and H^* , (c) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CHOH}^*$ (INT1; pathway I) and H^* , (h) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CH}_2\text{O}^*$ (INT1; pathway II) and H^* , (d) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CH-HOH}^*$ (TS2; pathway I), (i) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CH}_2\text{O-H}^*$ (TS2; pathway II), (e) & (j) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CH}_2\text{OH}^*$, (l) $(\text{C}_6\text{H}_5)\text{CHC-HHCHO}^*$ (TS1; pathway III) and H^* , (q) $(\text{C}_6\text{H}_5)\text{C-HHCHCHO}^*$ (TS1; pathway IV) and H^* , (m) $(\text{C}_6\text{H}_5)\text{CHCH}_2\text{CHO}^*$ (INT1; pathway III) and H^* , (r) $(\text{C}_6\text{H}_5)\text{CH}_2\text{CHCHO}^*$ (INT1; pathway IV) and H^* , (n) $(\text{C}_6\text{H}_5)\text{C-HHCH}_2\text{CHO}^*$ (TS2; pathway III), (s) $(\text{C}_6\text{H}_5)\text{CH}_2\text{C-HHCHO}^*$ (TS2; pathway IV), and (o) & (t) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_4\text{CHO}^*$. The purple, blue, and green colors represent Ru, Mo, and P atoms, respectively.

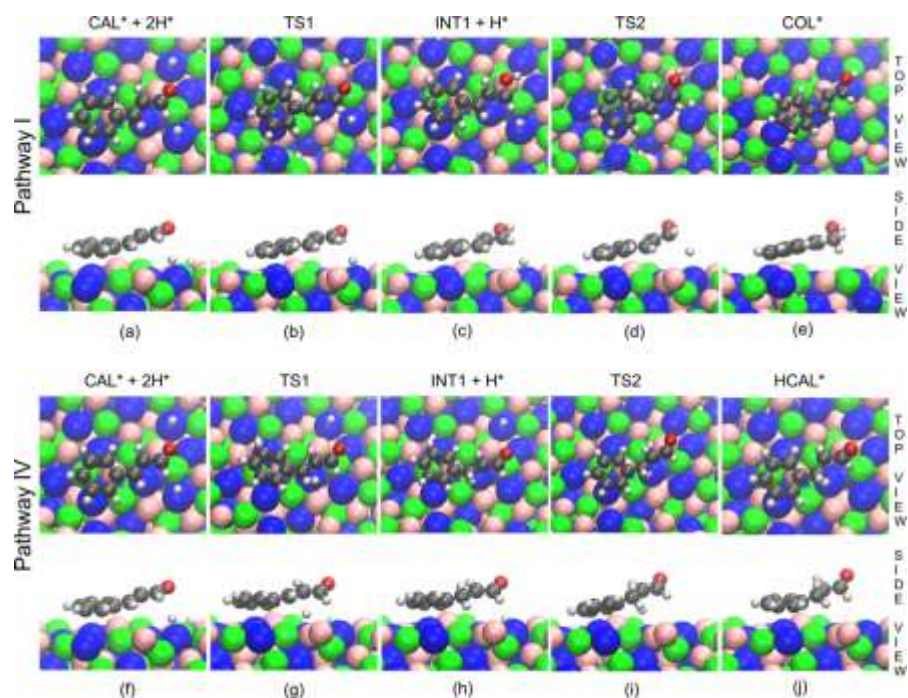


Figure A.19. Optimized structures of CAL, COL, HCAL, and reaction intermediates on the (111) facet of NiMoP during COL and HCAL reaction pathway (via pathway I & IV): (a) & (f) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CHO}^*$ and 2H^* , (b) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CHO}-\text{H}^*$ (TS1; pathway I) and H^* , (g) $(\text{C}_6\text{H}_5)\text{CHC}-\text{HHCHO}^*$ (TS1; pathway I) and H^* , (c) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CHOH}^*$ (INT1; pathway I) and H^* , (h) $(\text{C}_6\text{H}_5)\text{CHCH}_2\text{CHO}^*$ (INT1, pathway IV) and H^* , (d) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CH}-\text{HOH}^*$ (TS2; pathway I), (i) $(\text{C}_6\text{H}_5)\text{C}-\text{HHCH}_2\text{CHO}^*$ (TS2; pathway IV), (e) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_2\text{CH}_2\text{OH}^*$, and (j) $(\text{C}_6\text{H}_5)\text{C}_2\text{H}_4\text{CHO}^*$. The pink, blue, and green colors represent Ni, Mo, and P atoms, respectively.

TABLE A.1.
THE CRYSTALLOGRAPHIC INFORMATION OF MMOP

	Space group	a (Å)	b (Å)	c (Å)	Card reference	Crystallite size (nm)
FeMoP	Pnma (62)	5.922	6.790	3.663	04-001-4637	38 (112)
CoMoP	Pnma (62)	5.827	6.780	3.711	01-071-0478	51 (112)
NiMoP	P62m (189)	5.861	-	3.704	04-001-4648	31 (111)
RuMoP	Pnma (62)	6.035	6.944	3.853	04-015-7732	26 (112)

TABLE A.2.
ELECTRONEGATIVITY VALUES USED IN $\Delta\chi$ CALCULATION

Electronegativity scale	Electronegativity (eV)					
	Mo	Fe	Co	Ni	Ru	P
Allred-Rochow ²	1.30	1.64	1.7	1.75	1.42	2.06
Pauling ³	2.16	1.83	1.88	1.91	2.20	2.19
Mulliken ⁴	7.09	7.90	7.88	7.64	7.36	10.49

TABLE A.3.
CELL PARAMETERS FOR $\text{Ru}_x\text{Mo}_{2-x}\text{P}$ CALCULATED FROM RIETVELD
REFINEMENT (EXPERIMENTAL) AND COMPUTATIONALLY USING 1 X 4 X 2
SUPERCELL VIA OPTB88-VDW FUNCTIONAL.

cell parameter (Å)	$\text{Ru}_{1.2}\text{Mo}_{0.8}\text{P}$		$\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$		$\text{Ru}_{0.8}\text{Mo}_{1.2}\text{P}$	
	Exp.	Comp.	Exp.	Comp.	Exp.	Comp.
<i>b</i>	13.46	13.32	15.41	15.45	15.65	15.58
<i>c</i>	13.72	13.68	13.88	13.85	14.23	14.25

TABLE A.4.
SUMMARY OF MATERIAL COMPOSITION DETERMINED WITH ICP-OES
AND XPS NORMALIZED TO THE AMOUNT OF P.

Entry	Material	ICP-OES			XPS		
		Ru	Mo	P	Ru 3 <i>p</i>	Mo 3 <i>d</i>	P 2 <i>p</i>
1	MoP		1.0	1.0	-	1.1	1.0
2	Mo ₃ P		3.0	1.0	-	2.9	1.0
3	RuP	1.0		1.0	1.0	-	1.0
4	Ru ₂ P	1.9		1.0	1.8	-	1.0
5	$\text{Ru}_{0.8}\text{Mo}_{1.2}\text{P}$	0.8	1.2	1.0	0.7	1.3	1.0
6	$\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$	1.0	1.0	1.0	1.0	1.0	1.0
7	$\text{Ru}_{1.2}\text{Mo}_{0.8}\text{P}$	1.2	0.8	1.0	1.2	0.7	1.0

TABLE A.5.

REACTION RATE CONSTANT VALUES FOR ALL CATALYSTS.

	k_1 (h^{-1})	k_2 (h^{-1})	k_3 (h^{-1})	R^2 , k_2 vs. k_3
MoP	0.029	0.0035		
RuP	0.030	0.0013	0.0185	0.922
Ru ₂ P	0.027	0.0002	0.1752	0.949
Ru _{0.8} Mo _{1.2} P	0.078	0.0106		
Ru _{1.0} Mo _{1.0} P	0.176	0.0050	0.0039	0.977
Ru _{1.2} Mo _{0.8} P	0.258	0.0035	0.0134	0.971

TABLE A.6.

XPS BINDING ENERGY SHIFT AND XANES ADSORPTION ENERGY OF MONOMETALLIC MO PHOSPHIDES AND RU PHOSPHIDES.

Material	Binding energy (eV)			Adsorption energy (eV)	
	Ru 3p _{3/2}	Mo 3d _{5/2}	P 2p _{3/2}	Ru K-edge	Mo K-edge
MoP	-	228.2	129.5	-	20,001.25
Mo ₃ P	-	227.5	129.1	-	20,000.61
RuP	461.8	-	129.6	-	-
Ru ₂ P	462.0	-	129.4	22,117.42	-

TABLE A.7.
BADER CHARGE CALCULATIONS ON (112) AND (210) FACET OF
RU_{1.0}MO_{1.0}P

Atom	Bader charges (eV)	
	(112) facet	(210) facet
Ru	-0.23	-0.25
Mo	+0.70	+0.71
P	-0.46	-0.46

TABLE A.8.
SURFACE AND BULK BADER CHARGES OF MONOMETALLIC AND
BIMETALLIC PHOSPHIDES.

Material	Surface charges (e)			Bulk charges (e)		
	Ru	Mo	P	Ru	Mo	P
MoP	-	+0.52	-0.52	-	+0.52	-0.52
Mo ₃ P	-	+0.91	-0.91	-	+0.30	-0.91
RuP	+0.11	-	-0.11	+0.11	-	-0.11
Ru ₂ P	+0.13	-	-0.13	+0.06	-	-0.13

NOTE: The surface charges are calculated as the sum of Bader charges of one atom on the top-most layer. The bulk charges are the sum of Bader charges present in the total layers of catalytic system or supercell.

TABLE A.9.

PERPENDICULAR DISTANCE (D , Å) OF CARBON AND OXYGEN ATOMS OF CARBONYL GROUP OF TRANS-FURFURAL AND CENTER OF MASS (COM) OF FURANIC RING FROM THE SURFACE AFTER HORIZONTAL ADSORPTION ON (112) FACET OF $\text{Ru}_{0.8}\text{Mo}_{1.2}\text{P}$, RuMoP , AND $\text{Ru}_{1.2}\text{Mo}_{0.8}\text{P}$ CATALYSTS.

Atom	$\text{Ru}_{0.8}\text{Mo}_{1.2}\text{P}$	$\text{Ru}_{1.0}\text{Mo}_{1.0}\text{P}$	$\text{Ru}_{1.2}\text{Mo}_{0.8}\text{P}$
C	1.35	1.31	2.22
O	1.71	1.51	2.33
COM	1.73	1.68	3.51

TABLE A.10.

TEXTURAL PROPERTIES OF MONOMETALLIC AND BIMETALLIC CO, NI, RU, AND MO PHOSPHIDES.

Materials	H_2 uptake (mmol/g)	N_{CO} ($\mu\text{mol/g}$)	S_{BET} (m^2/g)
Co_2P	524	6.4	5.2
Ni_2P	430	7.5	5.5
Ru_2P	414	21	6.1
RuP	525	18	5.6
MoP	401	28	20
CoMoP	540	12	3.5
NiMoP	389	22	4.5
RuMoP	446	26	8.2

TABLE A.11.
BULK COMPOSITION FROM ICP-OES.

	Co	Ni	Ru	Mo	P
Co ₂ P	1.98				1.00
Ni ₂ P		1.92			1.00
Ru ₂ P			1.95		1.00
RuP			0.99		1.00
MoP				0.98	1.00
CoMoP	0.99			1.00	1.00
NiMoP		0.97		0.99	1.00
RuMoP			0.95	1.00	1.00

TABLE A.12.
AVERAGE PARTIAL CHARGES (Q , $|E|$) OF EACH TYPE OF SURFACE
ATOM ON RUMOP (112) AND NIMOP (111) FACETS.

Catalyst	Ru/Ni	Mo	P
RuMoP	-0.23	+0.70	-0.46
NiMoP	-0.04	+0.68	-0.64

TABLE A.13.

BINDING ENERGIES (E_{BE} , EV) OF CAL ((C₆H₅)C₂H₂CHO*), COL ((C₆H₅)C₂H₂CH₂OH*), HCOL ((C₆H₅)C₂H₄CHO*), AND HCOL ((C₆H₅)C₂H₄CH₂OH*) ON RUMOP (112) AND NIMOP (111) FACETS.

Catalyst	CAL	COL	HCOL	HCOL
RuMoP	-2.24	-1.44	-1.65	-2.16
NiMoP	-2.02	-1.58	-1.45	-1.98

TABLE A.14.

CHANGE IN PARTIAL ATOMIC CHARGE (Q , |E|) ON THE ATOMS OF CAL ((C₆H₅)C₂H₂CHO*), COL ((C₆H₅)C₂H₂CH₂OH*), HCOL ((C₆H₅)C₂H₄CHO*), AND HCOL ((C₆H₅)C₂H₄CH₂OH*) AFTER BINDING ON RUMOP (112) AND NIMOP (111) FACETS.

Atom	RuMoP				NiMoP			
	CAL	COL	HCOL	HCOL	CAL	COL	HCOL	HCOL
O ₁	0.35	0.05	0.07	0.17	0.30	0.02	0.15	0.05
C ₁	0.12	0.00	0.05	0.08	0.13	0.04	0.12	0.15
C ₂	0.21	0.02	0.23	0.04	0.19	1.41	0.03	0.04
C ₃	0.12	0.09	0.20	0.13	0.34	1.56	0.07	0.03
C ₄	0.02	0.11	0.05	1.64	0.03	0.10	0.06	0.03
C ₅	1.21	0.14	0.16	0.28	0.14	0.03	0.05	0.04
C ₆	2.92	0.15	0.23	0.32	0.22	0.01	0.02	0.11
C ₇	1.19	0.15	0.01	0.08	0.11	0.17	0.02	0.13
C ₈	0.43	0.17	0.13	0.56	0.01	0.14	0.21	0.01
C ₉	0.11	0.00	0.02	1.98	0.14	0.06	0.17	0.09

TABLE A.15.

THE PERPENDICULAR DISTANCE (d , Å) OF CARBON AND OXYGEN ATOMS OF CAL ((C₆H₅)C₂H₂CHO*), COL ((C₆H₅)C₂H₂CH₂OH*), HCOL ((C₆H₅)C₂H₄CHO*), AND HCOL ((C₆H₅)C₂H₄CH₂OH*) FROM THE SURFACE AFTER BINDING ON (112) FACET OF RU_{0.8}MO_{1.2}P_{1.0}, RU_{1.0}MO_{1.0}P_{1.0}, AND RU_{1.2}MO_{0.8}P_{1.0} CATALYSTS.

Atom	RuMoP				NiMoP			
	CAL	COL	HCOL	HCOL	CAL	COL	HCOL	HCOL
O ₁	1.94	4.64	3.74	1.80	3.85	4.40	4.64	4.57
C ₁	2.61	3.34	3.06	2.72	3.32	3.27	3.61	3.96
C ₂	2.39	3.28	2.89	2.29	3.15	2.94	3.40	3.91
C ₃	2.84	2.93	2.11	2.79	2.51	2.75	2.81	3.36
C ₄	2.66	2.69	1.91	2.42	2.18	2.42	2.21	3.17
C ₅	2.66	2.58	1.46	2.07	1.83	2.17	1.85	2.66
C ₆	2.42	2.35	1.51	1.88	1.81	1.86	1.80	2.34
C ₇	2.22	2.21	1.94	2.05	2.09	1.74	2.07	2.54
C ₈	2.23	2.27	2.26	2.37	2.38	1.98	2.37	3.10
C ₉	2.40	2.51	2.22	2.52	2.37	2.32	2.40	3.41