Screening of Molybdenum, Iron and Phosphorus based catalysts for hydrodeoxygenation of Simulated bio-oil as a model liquid product from fast pyrolysis

Master's thesis in Chemical Engineering Supervisor: De Chen Co-supervisor: Kumar Ranjan Rout, Kishore Rajendran, Petter Tingelstad July 2021

Norwegian University of Science and Technology Faculty of Natural Sciences Department of Chemical Engineering



Leo Gosbert Mboyerwa

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Preface

This Master's thesis was written during Spring 2020 at the Department of Chemical Engineering, Norwegian University of Science and Technology.

I would like to give my sincere thanks to my supervisor Professor De Chen, and my co-supervisor PhD candidate Kishore Rajendran for advice and guidance throughout this project. I would also like to thank my co-supervisors Senior Researcher Kumar R. Rout, and PhD candidate Petter Tingelstad for their contribution.

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Thank you,

19th July 2021,

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Abstract

Nine different catalysts were tested for hydrodeoxygenation (HDO) of simulated bio-oil which is comprised of a mixture of distill water, acetic- acid, acetol, furfural, phenol, guaiacol and eugenol. The tested catalysts include MoFeP, MoFeP/Al₂O₃, MoFeP/SiO₂, MoO₃/Al₂O₃, MoO₃/SiO₂, FePO₄/Al₂O₃, FePO₄/SiO₂, Ru-MoFeP/Al₂O₃ and Ru-MoFeP/SiO₂. The reaction conditions for all testing experiments were, temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1. The experiments showed that the catalysts had significant activity towards all the reactants, except phenol, which was the most difficult component to show conversion. The activity of catalysts followed the order Ru-MoFeP/Al₂O₃ > Ru-MoFeP/SiO₂ > MoO₃/Al₂O₃ > MoO₃/SiO₂ > MoFeP/Al₂O₃ > MoFeP/SiO₂ > MoFeP > FePO₄/Al₂O₃ > FePO₄/SiO₂, indicating that Ru-promoted MoFeP based catalyst can highly hydrogenate phenol's aromatic ring. On the contrary, the FePO₄ based catalyst showed the least activity among all.

Overall, the project is mostly targeted towards synthesis, characterization and application of MoFeP based, MoO₃ based and FePO₄ based catalysts, that have been studied for application under industrially relevant conditions. By using simulated bio-oil as feedstock, the Ru cluster promoted catalyst showed remarkable selectivity to C-O phenolic bonds cleavage, towards high yield of biofuel production. A significant hydrodeoxygenation degree was observed for the Ru-promoted catalyst as compared to bulk and supported MoFeP catalysts.

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1. Introduction

The rising economic development that facilitates globalization has caused a remarkable increase in energy demand. Currently, fossil fuel accounts for about 80% of the global energy consumption and 95% of the transport energy demand [1]. As fossil fuel resources become more limited, the ability to use alternative feedstocks to supplement current liquid transportation fuels production and subsequent reduction of CO₂ emissions becomes critical. One among several solutions towards solving this existing problem is by utilization of biomass.

Currently, the production of biodiesel and bio-ethanol based on food-grade biomass have been commercialized and they contribute up to 4% of total fuel consumption [2]. This has led to a rise of ethical issues because food supply must compete with fuel production while some parts of the world struggle by having a limited supply of food. Hence, it is necessary to divert into the utilization of non-edible biomass sources to prevent competition with food supply. Therefore, to fully realize the potential of lignocellulosic biomass as a feedstock for fuel production is essential.

Lignocellulose biomass contains cellulose, hemicellulose and lignin. All the components of lignocellulosic biomass contain a C–O bond, which is an important and frequently observed functionality that provides a junction point for the propagation of carbohydrates or monolignols [3]. One cheap and feasible method that is proposed for the utilization of lignocellulose biomass is hydropyrolysis. Hydropyrolysis is a special form of fast pyrolysis, which is an endothermic decomposing of biomass to bio-oil in a hydrogen atmosphere with a short vapour residence time of 1-3 seconds, and takes place within a temperature range of 500-650°C [4]. Decomposition of lignocellulose biomass results into bio-oil, which contains aromatic compounds mostly originated from lignin [5]. Furthermore, the oil also contains oxygenates of C_1 - C_6 carbon length, such as acetic acid, acetol, anhydrous-sugar, furan, alcohol and carbonyls like ketone and aldehyde, which originate from cellulose and hemicellulose components. These components result in overall high oxygen content of pyrolysis oil leading to high acidity, increased viscosity and phase separation of the oil [6]. On top of that, high oxygen and water content of pyrolysis oil compared to fossil fuel, results in lower heating values (15–19 MJ/kg) compared to fossil fuels (40 MJ/kg) [7]. Lignin has become an attractive source of gasoline-range hydrocarbons due to its large aromatic content and

oxygen to carbon ratio compared to cellulose and hemicellulose [8]. Nevertheless, this has been limiting because of the high amount of aryl ethers and phenolic compounds present in bio-oils produced from lignocellulosic biomass. To remove oxygen from bio-oil, catalytic hydrodeoxygenation is required. The phenolic C–O bond energy is large (468 kJ/mol) and makes the direct hydrodeoxygenation difficult. It therefore requires several conditions which favors C-O bond cleavage resulting to selectivity towards production of aromatic compounds [9].

Several studies involved catalysts such as MoS_2/Al_2O_3 promoted with Ni [10], that are known to be active and selective for hydrodesulfurization of petroleum oils, for hydrodeoxygenation. Nevertheless, sulfiding agents like H₂S must be added to the hydrodeoxygenation reactor to maintain adequate sulfidation of the catalyst regardless of bio-oils being sulfur-free. This is undesirable and, therefore, an alternative non-sulfided catalyst was of interest. A comparative study made by Stinner et al., [11] showed that turnover frequency shown by MoP was approximately 6 times higher than MoS_2/Al_2O_3 for the hydrodenitrogenation of orthopropylaniline, based on geometric estimates of surface site density. Other studies reported metal phosphides as being more active and selective than sulfided metals for HDS and HDN. Philips et al [12] showed that MoP/SiO_2 has four times the activity of MoS_2/Al_2O_3 for the HDS of thiophene. Therefore, the use of metallic phosphide catalysts needs to be further studied.

In this project, more study on MoFe phosphide was of interest because of the results obtained from previous studies. Rensel et al. [3], reported MoFeP catalyst to have selectivity as high as 90% benzene and 10% cyclohexane at the hydro-processing temperature of 400°C and industrially low pressure of 2.1MPa of H₂ at near-complete conversion, approximately above 99%. A study by Bonita and Hicks [13], showed that complete deoxygenation of phenol to benzene, cyclohexane, and cyclohexene was accomplished using RuMoP and FeMoP compared to CoMoP and NiMoP. Moreover, Rensel et al [14] showed that MoFeP showed enhanced turn over frequencies exhibited by greater Lewis acid sites, which reduce the activation energy required to cleave the C-O bond of phenol. Rensel et al [15] also reported that MoFeP exhibited excellent stability, which was evidenced by the retention of the initial reaction rate, selectivity to benzene, and oxidation state of surface species throughout the time-on-stream run.

Despite promising results obtained on MoFeP for hydrodeoxygenation reaction, it is not immediately evident in what respects to the catalyst similarities to non-phosphide catalytic systems, due to lack of computational work on bimetallic phosphide catalysts. Therefore, this project is aimed at implementing preparation techniques that can give results similar to the performed density functional theory calculations done on MoFeP catalysts, to gain mechanistic insights into their activities[14]. The DFT results will be used to identify pure phases of the prepared MoFeP catalyst.

2. Literature Review

2.1. Biofuels

Biofuels are a type of fuel produced from biomass. Biomass, for most of history, has been the primary energy source powering human development. This energy supply has taken various forms, including wood and dung for cooking and heating, charcoal for metallurgy, and animal feeds for food and transportation [16]. In this project, the focus will be to produce biofuel from lignocellulosic biomass as feedstock, obtained from wood.

2.2. Lignocellulosic feedstock

Lignocellulosic biomass, which refers to plant and plant-derived matter produced by photosynthesis, is chemically composed of cellulose, hemicellulose, and lignin, and is the only renewable source of carbon on earth [17]. The polymer composition depends on the type of biomass. The composition range for lignocellulosic feedstock is 35-55% cellulose, 20-35% hemicellulose, and lignin accounting for about 10-30%. Cellulose and hemicellulose are polysaccharides originating from the cell walls in organic material. Degradation of these polymers results in various sugars, acids, alcohols, and furans. Lignin, on the other hand, is a complex structure that makes it difficult to extract from wood. This is the reason why it is not used to a large extent in the industry today. When lignin is decomposed, it produces aromatic oxygenates such as phenolics and guaiacols in bio-oil [18].

2.3. Fast pyrolysis

Pyrolysis is a thermal decomposition occurring in the absence of oxygen [19]. Main products from pyrolysis are organics, water, char and gas. Production of charcoal is favoured by lower process temperatures and longer vapour residence times. While biomass conversion to gas is favoured by high temperatures and longer residence time. Production of liquids is facilitated by

moderate temperatures and short vapor residence time. **Error! Reference source not found.** shows a summary of product distribution from different pyrolysis modes.



Figure 2.1: Product spectrum from pyrolysis

This project is focused on fast pyrolysis because the liquid is the most desirable product. Fast pyrolysis produces a liquid fraction up to 75 wt% due to the very short (1-2 s) residence time. To reduce the oxygen content of the bio-oil product within a single step process, some attention has returned to the concept of integrating pyrolysis and hydrocracking, in which hydrogen is added to the pyrolysis reactor [19]. This process is termed as Hydropyrolysis.

Hydropyrolysis has some contrasting requirements such as high pressure in pyrolysis increases char yields as shown by Antal [20] and reduces liquid yields, at the same time, high pressures are required to provide effective hydrogenation. Overall, the important role of hydrogen in hydropyrolysis is to enhance the polymerization of poly-aromatics, olefins and other anhydrous oligosaccharides [21], increasing the rate of cracking reaction and reduction of coke deposition [22].

2.4. Upgrading of bio-oil

Upgrading of bio-oil is essential to eliminate the undesired physical and chemical properties of biooil. The properties include low heating value, high instability, and tendency to polymerize during storage, high acidity and corrosion and high-water content. Low heating value and high acidity are mainly due to the high content of oxygenated compounds in bio-oil [23]. This further creates a challenge in the transportation and storage of biofuel. Upgrading is therefore necessary to remove water and oxygen from bio-oil [24].

Bio-oil consists of several organic compounds such as alcohols, acids, aldehydes, ketones and esters [25]. The composition depends on biomass feedstock and pyrolysis conditions [4]. Catalytic upgrading of bio-oil can be achieved by applying different strategies. These include several reactions such as cracking, alkylation, isomerization, condensation, hydrodeoxygenation, etc. as illustrated in Figure 2.2 below. The attractive strategy for bio-oil upgrading is to convert low to high molecular weight oxygenates followed by hydrodeoxygenation [26]. In this project, the focus will be on hydrodeoxygenation.



Figure 2.2: Reactions associated with bio-oil upgrading [27]

Hydrodeoxygenation is a reaction for selectively removing oxygen from compounds using hydrogen. Equation (1) below shows the general reaction of hydrodeoxygenation. It is an exothermic reaction that is usually carried out at a temperature range of 127-500°C and high hydrogen partial pressure.

$$Oxygenates + H_2 \xrightarrow{\longrightarrow} Cat. Deoxygenated hydrocarbons + H_2O$$
(1)

Understanding the reaction mechanism, reactants, and products of hydrodeoxygenation is important for the design and optimization of the catalyst. Bio-oil that originates from lignocellulosic biomass is reported to have a high content of oxygenated aromatics [28]. These include 4- methoxyphenyl, dimethylphenol, syringol, and catechol. Phenols undergo hydrodeoxygenation by removing the OH group due to C-O-cleavage to produce benzene and water. Selective hydrodeoxygenation of lignocellulose derived bio-oil requires less hydrogen compared to lignin-derived bio-oil.



Figure 2.3: Selective hydrodeoxygenation and selective hydrogenation

In addition to phenols, other components in bio-oil that will be studied in this project for hydrodeoxygenation include acetic acid, acetol, furfural, iso-eugenol and guaiacol. Acetic acid enhances acidity and corrosion in bio-oil [29]. Therefore, the deoxygenation of acetic acid to ethane

is highly desirable. Acetol is fully deoxygenated to propane [30] while products such as CO₂ and C1-C3 occur due to cracking [31]. Guaiacol undergoes several reactions such as deoxygenation, demethylation and transfers reactions to produce benzene or various substituted aromatics [32]. Iso-eugenol undergoes similar reactions as guaiacol with additional dealkylation [33]. Furfurals produce different products depending on the interaction between the furan ring and the metal catalyst, which results in ring-opening and rearrangements [34]. The reaction pathway of components may vary by changing reaction conditions [35].



Figure 2.4: Organic compounds mixed to synthesize Simulated Bio-oil used in activity studies in this project.

2.5. Catalysts for hydrodeoxygenation

To design the optimal catalyst for hydrodeoxygenation, several factors such as reaction mechanism, optimal reaction conditions, stability, coke resistance and cost must be considered. Based on the hydrodeoxygenation mechanism, the designed catalyst should be able to perform both hydrogenation and subsequent C-O bond cleavage. The active site on the catalyst is responsible for hydrogenation while the acid sites in the catalyst are responsible for C-O scission. The overall mechanism entails the presence of active sites capable of activating hydrogen close to sites that are effective for C-O bond cleavage and then the presence of acidic sites to facilitate the dehydration[36]. Several studies have been done to investigate different catalysts for hydrodeoxygenation. Some catalysts studied include Pt/Al₂O₃ [37], Ni-Mo/SiO₂ [38], Pd-Fe/carbon [38] and many others. In this project, the focus will be on transition metal phosphides, based on Molybdenum and Iron metals.

2.6. Transition metal phosphides

Transition metal phosphide is a catalyst category which seems to be promising for hydrodeoxygenation. It contains catalysts with both acidic sites and active transition metals [3]. Various experiments performed by phosphides provide promising results as applied to hydrodeoxygenation. Hydrodeoxygenation of anisole(methoxybenzene) which was done by Li et al., [39] over Ni₂P, MoP, and MoNiP catalyst with silica support concluded that increasing Ni/Mo ratio in the catalyst increased the activity for the hydrodeoxygenation of anisole. Also, the NiP catalyst showed higher activity compared to a conventional NiMo/Al₂O₃ catalyst.

A study by Romero et al., [40] showed that hydrodeoxygenation of benzofuran over MoNiP/Al₂O₃ catalyst resulted in 2-ethylphenol as the main product. Subsequent deoxygenation resulted in cyclohexane as well as ethylbenzene. Consequently, the further reaction of 2-ethylphenol was inhibited by benzofuran indicating the complexity and challenges of upgrading real bio-oil.

A study by Tymchsyn et al., [41] where MoCoP/Al₂O₃ catalyst was used for the upgrading of glycerol, concluded that acidic materials were effective for deoxygenation reactions. Most products were alkylated phenols and ketones. The incorporation of phosphorous proved to inhibit coke

formation at 300°C and hydrogen partial pressure of 50 bar reaction conditions as well as enhancing hydrodeoxygenation.

Hydrodeoxygenation mechanism over transition metal phosphides as proposed by Kelun [39], explains that hydrogen is first adsorbed and activated by the transition metal forming hydrogen atoms. Then, the oxygenated compound adsorbs on a nearby transition metal site to form an oxygen-metal-bond intermediate. The intermediate further reacts with activated hydrogen, which forms incomplete oxidation of phosphide to produce a deoxygenated product and water. The mechanism does not explain the effect of the support, but different oxygenated can adsorb on different sites of the support to give different product.

Despite the promising results of MoFeP catalyst on hydrodeoxygenation, there is not enough computational work done on the challenges of MoFeP phase. Rensel et al. [14], performed density functional theory (DFT) calculations to gain mechanistic insights into the activity of MoFeP catalysts and to understand how phenol interacts with the various catalytic surfaces in the catalyst during hydrodeoxygenation.

2.7. Catalyst supports

The support in the catalyst is used in order to increase dispersion and stability of the active material [42]. The active material will attach itself within the pores of the support and hence improve the interaction with the reactant. Sometimes the supports also participate in the reaction itself or promote the reactivity of the active material. Commonly used supports and commercially available are silica, alumina and carbon. Alumina is widely used because of better thermal and mechanical stability. Silica is mostly used at temperatures lower than 300°C during hydrogenation or oxygenation reactions. However, carbon is used when active material are noble metals [42]. During hydrodeoxygenation reaction, γ -Al₂O₃ offers Lewis acidity and high surface area for the dehydration step.

2.8. Catalyst Synthesis

2.8.1. The Pechini Method

The Pechini method is a catalyst preparation technique that is often preferred when the catalyst contains several organic oxides [43]. This method enables good control of the cation stoichiometry in the component mixture and ensures a high degree of homogeneity [44]. The preparation involves mixing the catalyst precursors with an aqueous acidic solution. The acidity in the solution prevents the immediate precipitation of the components. Citric acid is usually used in most cases [45].

2.8.2. Incipient wetness impregnation

Incipient wetness impregnation is also known as capillary impregnation or dry impregnation method [46]. This method applies to the synthesis of supported catalysts. The method involves the determination of the total pore volume of the support, which will be used to determine the amount of solvent required to dissolve the required amount of loading-metal salt precursors. The support material is then mixed with the metal precursor solution in a dropwise manner until saturation. The obtained substance is then dried to obtain a solid raw material.

2.8.3. Calcination

Calcination is the process that involves the activation of a catalyst at high temperatures in the presence of oxygen or airflow. Calcination parameters such as temperature, dwell time and heating rate determines the structure formation, surface area and physio-chemical properties of the catalyst [47]. Although, very high calcination temperatures may lead to sintering of loaded metal in the catalyst. The stability of the catalyst depends on calcination at relatively high temperatures compared to normal reaction temperatures.

2.8.4. Reduction

Reduction of catalyst is done to reduce the oxidation state of the active metal site of the catalyst. In most cases, a catalyst is reduced in a reactive atmosphere such as hydrogen. Reduction in temperature and heating rate determine the final performance of the catalyst [48]. In transitional metal phosphide catalyst, the reduction is applied to reduce phosphates into phosphides, which require high temperature. To hinder re-oxidation of the catalyst, the catalyst is passivated at a low concentration of oxygen in an inert gas to form a protective oxide layer on the catalytic surface.

2.9. Characterization

The physical and chemical properties of the catalyst can be explained through characterization [42]. The catalyst can be further improved and optimized using characterization techniques.

2.9.1. X-ray diffraction

In catalyst characterization, diffraction patterns are mainly used to identify the crystallographic phases that are present in the catalyst. X-ray diffraction occurs in the elastic scattering of X-ray photons by atoms in a periodic lattice. The scattered monochromatic X-rays that are in phase give constructive interference [49]. Bragg's relation (2) can determine the spacing between two lattice planes. This spacing is characteristic for a specific phase [50]:

$$n\lambda = 2dsin\theta; \quad n = 1, 2, \dots \tag{2}$$

where λ is the wavelength of the X-rays, d is the distance between two lattice planes, θ is the angle between the incoming X-rays and the normal to the reflecting lattice plane, and n is an integer called the order of the reflection [49]. The limitation of XRD is that it cannot detect particles that are either too small or amorphous. Hence, one can never be sure that there are no other phases present than the ones detected with XRD.

2.9.2. Scanning Transmission Electron Microscopy (STEM)

Scanning Transmission Electron Microscopy (STEM) is a technique used to investigate the morphology of the catalysts. In STEM, the beam is condensed down to a very small spot, only a nanometer or so across [51]. The small spot is then scanned over an area of interest and the image is formed pixel by pixel during the scan. Electrons that interact strongly with the sample are deflected and then detected by a High Angle Annular Dark Field (HAADF) detector. The electrons that hit the HAADF detector are used to create a picture like a dark field image in which thicker regions or regions with elements with higher atomic number, appear brighter. It is relatively insensitive to sample orientation (unlike Bright Field and Dark Field imaging) because it collects electrons scattered to larger angles that contain less orientational information. STEM can be very useful because the very small beam can be used to probe specific areas with other analytical techniques, such as Energy Dispersive X-Ray spectroscopy (EDX).



Figure 2.5: A simplified diagram of a TEM in STEM mode. The scattered electrons are detected by a circular HAADF detector and then used to create an image [51].

2.9.3. Energy Dispersive X-Ray Spectroscopy (EDX)

Energy Dispersive X-Ray spectroscopy (EDX) extracts information about the elements that compose a catalyst [52]. High energy electrons in the main beam can knock inner orbital electrons away from atoms in the sample. Other electrons can then fall into these holes and the energy lost as they fall into these potential wells is carried away by an X-ray. The energy of the X-rays corresponds to the size of the potential well that the electron has fallen into and is characteristic of individual elements. Each element has different energy levels, and the X-rays can be used to identify elements present in the catalyst. A detector in the microscope can sense the energy of each X-ray that is incident upon it, and create a graph of the results, like in the Figure 2.6 below. The computer can then label the peaks according to the energy of the X-rays. A higher the number of counts indicates a greater the presence of a particular element. Multiple peaks per species are a result of electrons being knocked out of different orbitals or the initial orbital being refilled by electrons from different higher energy orbitals. When the microscope is in STEM mode, X-ray spectra can be obtained for specified areas of the image; while the X-ray detector is gathering data, the computer restricts the beam to the selected area.



Figure 2.6: A typical EDX spectrum, showing labeled peaks for Oxygen, Iron, Molybdenum, Phosphorus and Silica taken by S-5500 STEM-EDX

2.9.4. Line Scans

STEM and EDX can also be used to create line scans which create an elemental cross section of the sample along a user designated line [52]. The beam is controlled to stop at a given number of points along the line for a short amount of time. Line scans are only limited by the user's patience, specimen damage, or specimen drift. The data from each point can be collected and analyzed to graph the amount of a certain element at each point across the scan. This process shows how the number of different elements may be changing as the beam moves from one area of the same to another. Line scan illustration can be shown later in Catalyst Characterization section.

2.9.5. N₂-adsorption

The surface area of each sample was calculated using the Brunauer–Emmett–Teller (BET) method, and the pore size distribution and pore volume were characterized using the Barrett–Joyner–Halenda (BJH) method. The Brunauer-Emmett-Teller (BET) method is widely used to determine the surface area of porous materials. The model is based on the Langmuir isotherm and is mostly used in the linear form given in equation (3):

$$\frac{p}{n^{a}.(p^{o}-p)} = \frac{1}{n_{m}^{a}.C} + \frac{(C-1)}{n_{m}^{a}.C} \cdot \frac{p}{p^{o}}$$
(3)

where n^a is the amount adsorbed at the relative pressure p/p^o and n_m^a is the monolayer capacity. The monolayer capacity is usually defined as the amount of adsorbate (expressed in appropriate units) needed to cover the surface with a complete monolayer of molecules [53]. The BET equation requires a linear relation between $\frac{p}{n^a.(p^o-p)}$ and p/p^o (i.e. the BET plot). The range of linearity is, however, restricted to a limited part of the isotherm, usually not outside the p/p^o range of 0.05-0.30.

The calculation of the surface area (often termed BET area) requires a knowledge of the average area, a (molecular cross-sectional area), occupied by the adsorbate molecule in the complete monolayer.

Thus,

$$A_s(BET) = n_m^a . L. a_m \tag{4}$$

and

$$a_s(BET) = \frac{A_s(BET)}{m}$$
(5)

where $A_s(BET)$ and $a_s(BET)$ are the total and specific surface areas, respectively, of the adsorbent (of mass m) and L is the Avogadro's constant.

Mesopore size calculations are usually made with the aid of the Kelvin equation (6) in the form

$$\frac{1}{r_1} + \frac{1}{r_2} = -\frac{RT}{\sigma^{lg} \cdot v^l} \cdot \ln \frac{p}{p^o} \tag{6}$$

which relates the principal radii, r_1 and r_2 , of curvature of the liquid meniscus in the pore to the relative pressure, p/p° , at which condensation occurs. Hence σ^{lg} is the surface tension of the liquid condensate and v^l is its molar volume. It is generally assumed that this equation can be applied locally to each element of the liquid surface.

The hysteresis loops that arise due to adsorption-desorption behaviour were defined by IUPAC in different ways as shown in Figure 2.7 below. The Type I isotherm is commonly found in microporous substances such as zeolites and activated carbons. Whereby, the quantity of gas physisorbed is exclusively dependent on the accessible micropore volume rather than on the internal surface area. Type II isotherm is exhibited by microporous or non-porous adsorbents, which is caused by unrestricted monolayer-multilayer adsorption even at high relative partial pressure. The Type III isotherms is a result of weak gas-solid interaction and cluster formation of adsorbed molecules. However, the Type IV isotherm majorly differs from previous isotherms on the non-reversible nature of the adsorption and desorption pathways.



Figure 2.7: Physisorption isotherms and hysteresis loops proposed by IUPAC.

3. Experimental Section

3.1. Materials

All chemicals were used as received from the suppliers: ammonium phosphate dibasic $((NH_4)_2HPO_4, Sigma Aldrich, 99\%)$, iron nitrate nonahydrate (FeNO₃·9H₂O, Sigma Aldrich, 99%), ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄.4H₂O, Sigma Aldrich, 99%), Citric acid (Sigma Aldrich, 99%), and Sasol chemicals USA, LLC, Catalox ® alumina powder, RuCl₃ (Sigma Aldrich, 99%). Acetic acid, acetol, furfural, phenol, guaiacol and eugenol were all purchased from Sigma Aldrich with purity >99%.

3.2. Catalyst Synthesis

A total of 11 catalyst were synthesized and they were categorized according to Table 3.1 below:

| Category | Catalyst |
|--|--|
| | • MoO ₃ |
| Pure Phase | • FePO ₄ |
| | • MoFeP |
| | • MoO ₃ /Al ₂ O ₃ |
| | • $FePO_4/Al_2O_3$ |
| Supported catalysts; 20% active material on | • MoFeP/Al ₂ O ₃ |
| Al ₂ O ₃ or SiO ₂ | • MoO_3/SiO_2 |
| | • FePO ₄ /SiO ₂ |
| | • MoFeP/SiO ₂ |
| Ru Promoted catalysts | • Ru-MoFeP/Al ₂ O ₃ |
| Ru i fomoteu catalysts | • Ru-MoFeP/SiO ₂ |

Table 3.1: Synthesized catalysts

MoFeP was synthesized by the Pichini method, following a procedure from Rensel et al., study [14]. The FeNO₃·9H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, and (NH₄)₂HPO₄ precursors were added to an aqueous, citric acid solution (0.4 M) at a 1:1:1 molar ratio of Mo: Fe: P. A rotary evaporator was used to partially dry the mixture to a viscous solution. This was achieved at a temperature of 100°C in 24 hours by a process called ageing. The resulting gelatinous substance was then moved to a crucible bowl. The material was then dried in an oven at 110°C for 12 hours. The resulting brown solid was ground into a powder and calcined in an air atmosphere by ramping to 550 °C with a ramp rate of 1 °C min⁻¹ and holding at 550 °C for 6 hours. The resulting powder was reduced under a flow of H_2 with a rate of 160 mL min⁻¹ inside a quartz tube in a tube furnace. The following reduction procedure was employed: ramp to 100 °C at 5 °C min⁻¹ held at 100 °C for an hour, ramp to 260 °C at 5°C min⁻¹ held at 260 °C for an hour, and ramp to 720°C, 750 °C, 775°C or 800°C at 5°C min⁻¹ and held at the final temperature for 2 hours. After reduction, the resulting catalyst was cooled to room temperature under a hydrogen atmosphere, passivated using a 1% O_2 /He with the flow rate of 60 mL min⁻¹ for an hour, and stored inside a nitrogen dry box. MoFeP catalysts reduced at different temperatures were synthesized, that is, MoFeP_720, MoFeP_750, MoFeP_775 and MoFeP_800. Summary for MoFeP synthesis is illustrated in Figure 3.1 below.



Figure 3.1: Summary of preparation of MoFeP
MoO₃ was synthesized by direct calcination of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. The powder was calcined in an air atmosphere by ramping to 400°C with a ramp rate of 5°C min⁻¹ and holding at 400°C for 5 hours [54]. Summary for MoO₃ synthesis is illustrated in Figure 3.2 below.



Figure 3.2: Summary of MoO₃ preparation

FePO₄ was synthesized by the Pichini method where, FeNO₃·9H₂O and (NH₄)₂HPO₄ were precursors were added to an aqueous, citric acid solution (0.4 M) at 1:1 molar ratio of Fe:P. A rotary evaporator was used to partially dry the mixture to a viscous solution at 100°C and 24 hours, which was then moved to a crucible bowl. The material was then dried in an oven at 110°C for 12 hours. The resulting brown solid was ground into a powder and calcined in an air atmosphere by ramping to 550 °C with a ramp rate of 1 °C min⁻¹ and holding at 700 °C for 6 hours [3]. Summary for FePO₄ preparation is illustrated in Figure 3.3 below.



Figure 3.3: Summary of FePO₄ preparation.

Supported catalysts were prepared by the incipient wetness impregnation method. First, aqueous citric acid (0.4M), was prepared to create an acidic environment to free the metal salts from precipitating. Then, 1:1:1 or 1:1 molar concentrations of Mo:Fe:P or Fe:P respectively, were added stepwise into the prepared citric acid solution. In the case of MoO₃/Al₂O₃, (NH₄)₆Mo₇O₂₄·4H₂O was dissolved in the solution. The precursors were weighed to represent 20% wt loading of the active metal phase of the respective catalysts. The homogeneous solution obtained was then impregnated on alumina powder or silica gel. The obtained catalysts were then dried at 100°C for 12 hours. The catalysts were further calcined at conditions similar to their respective pure phases. MoFeP/Al₂O₃ and MoFeP/SiO₂ were further reduced and passivated at conditions similar to the pure MoFeP phase.

The Ruthenium promoted catalysts were synthesized by impregnating RuCl₃ on pre-calcined MoFeP/Al₂O₃ and MoFeP/SiO₂. The catalysts were pre-calcined in air at a heating rate of 1 °C/min to a temperature of 350 °C and dwell for 6 h. Ru at 1 wt % was then impregnated onto the calcined catalyst using the incipient wetness impregnation method. The Ru-promoted catalyst on MoFeP/Al₂O₃ and MoFeP/Al₂O₃ was subsequently dried 100 °C (4 h) and calcined at 500 °C using 1 °C/min heating rate, to remain at the final temperature for 5 h. The active phase, Ru-MoFeP, was obtained by reducing the catalyst at similar conditions as MoFeP.

3.3. Preparation of Simulated Bio-oil

The simulated bio-oil was prepared to in other to achieve similar characteristic as lignocellulosic derived bio-oil. The components include, distilled water, acetic- acid, acetol, furfural, phenol, guaiacol and eugenol at a weight fraction of 28.7, 12.3, 13.8, 10.6, 15.7, 9.1 and 10.4 %, respectively. The components were mixed in a flask and stirred for an hour. The prepared feedstock was then stored in a fridge at a temperature below 5°C. The acetic acid, acetol and furfural are decomposing products from holocellulose fraction of woody biomass while phenol, guaiacol and eugenol are monomers derived from lignin. Based on the calculated O/C and H/C ratios of the component mixture, it can be concluded that the simulated bio-oil has similar composition to bio oil derived from wood [55].

3.4. Activity measurement

Activity testing was carried out in a fixed bed reactor as shown in detailed piping and instrumentation diagram in Figure 3.4 below. The set-up was operated at same conditions for each catalyst, which is, temperature of 400°C, H₂ partial pressure of 14.7 bar and total pressure of 20 bar. Simulated bio-oil was fed into the reactor at the flow rate of 0.04ml/min using HPLC pump, and 0.4 grams of catalyst was used in the experiments. H₂ and N₂ flowrates were set to 220ml/min and 20 mL/min respectively to maintain the WHSV of 0.94h⁻¹.

The catalyst were in situ reduced in H₂ flow of 500 ml/min in N₂. The feed (simulated feed, Sigma Aldrich, 99.9%) was fed into the reactor by HPLC pump. The reactant and product concentration were measured by gas chromatography (Agilent 6890) using a phenyl methyl siloxane capillary column (Agilent HP-5, 40 m, 320 μ m ID, 0.25 μ m film) connected to FID and mass spectrometer (MSD 5977 E). Agilent GC/TCD-FID detector monitored the gas phase products. The condensed liquid phase product mixture (aqueous and organic phases) were analyzed by a GC-FID (Agilent 6890-5977E) with a mass spectrometer detector. Products were identified by NIST11 MS libraries. The peaks with the same molecular weight (Mw) were unified and their structure pre-determined by GC-MS. Quantitative analysis of the liquid phase products were based on one-dimensional GC-FID analysis (Agilent 7020). The calculation of conversion and selectivity was done similar to [56].



Figure 3.4: Pipping and instrumentation set-up for activity testing.

4. Results and discussion

4.1. Catalyst Characterization

X-ray diffraction was used to determine the bulk phases present in synthesized catalysts. The results of MoFeP, MoO₃ and FePO₄ after calcination were shown in Figure 4.1 below. From XRD, the bimetallic mixture was composed of both MoO₃ and FePO₄ phases based on XRD patterns matched to MoO₃(JCPDF 00-005-0508) and FePO₄(JCPDF 00-029-0715). Rensel et al., [3] combined the EDS and SEM images of FePO₄, MoPO₄ and MoO₃ and reported that two distinct phases formed instead of one combined phase, where, it appeared that the FePO₄ crystals envelop the MoO₃ phase. We may therefore conclude that this mixture of FePO₄ and MoO₃ was used to synthesize FeMoP through further reduction with hydrogen.



Figure 4.1: XRD patterns of MoO₃, FePO₄ and mixture of (MoO₃+FePO₄) showing bulk crystal structure.

N₂-adsorption characterization was done to confirm results obtained in XRD for MoFeP catalyst. The nitrogen adsorption-desorption isotherm of calcined MoFeP shown in Figure 4.2 below exhibits a typical shape of a mesoporous material. As observed, a saturation bearing builds up at high relative pressure and this saturation corresponds to the activities of mesoporous materials. Besides, a clear hysteresis is observed between the adsorption and desorption curves corresponding to an irreversible adsorption-desorption phenomenon. The obtained isotherms are typical type IV isotherms, according to the IUPAC classification. The hysteresis loop at relative pressure higher than 0.6 indicates that large pores from mesopores to macropores are present in the calcined MoFeP.



Figure 4.2: N₂ desorption-adsorption isotherm of calcined MoFeP

The physical characteristics deducted from the nitrogen adsorption-desorption isotherms of the samples synthesized in Table 4.1 below show that the pore volume of calcined MoFeP is about average the total pore volume of FePO₄ and MoO₃. This agrees with the results obtained from the XRD.

| Sample | BET* (m²/g) | Pore Volume (cm ³ /g) | Pore diameter(nm) | Average crystallite size(nm) |
|-------------------------------|----------------|--|----------------------|------------------------------------|
| MoFeP calcined at 550°C | 4.7 | 0.3 | 8 | 7 |
| FePO ₄ | 6.2 | 0.2 | 18 | 1 |
| MoO ₃ | 3.2 | 0.4 | 5 | 45 |

Table 4.1: Physical characteristics deducted from the treatment of nitrogen adsorption-desorption isotherms.

*BET specific surface area calculated by BET; total pore volume and pore size of the mesopores calculated by BJH.

The MoFeP catalyst was obtained by further reduction with varying reduction temperatures ranging from $720 \circ C$ to $800 \circ C$ to identify suitable temperature which produces pure phase without giving intermediate phases. The bulk crystal structures of the resulting MoFeP catalysts were investigated using X-ray diffraction (XRD). The XRD analysis was done to determine the suitable reduction temperature for the production of the crystalline MoFeP structure similar to the simulated structure obtained by Rensel et al., [14]. According to the previous study by Rensel et al., [15], the catalysts synthesized at $600 \circ C$ or below exhibited multiple diffractions attributed to bulk phases of Mo, MoO₂, MoO₃, FePO₄, and Fe₂PO₇. It was further reported that the catalysts synthesized at 650 °C or greater showed only diffractions assigned to the crystalline MoFeP bulk phase, and thus were utilized in this study. All the prepared catalysts showed diffractions assigned to the crystal planes of orthorhombic MoFeP (PDF No.: 04-001-4367), with the (112) facet as the most dominant plane as shown in Error! Reference source not found. below. This is in good agreement with the Fe_1Mo_1P phase computed by DFT calculations [14]. However, additional phases were observed in all catalyst which resulted due to several factors. MoP phase observed at 800°C is a result of crystalline growth as confirmed later by Crystalline size calculations done by the Scherrer equation. Fe₂O₃ phases observed at temperatures 750°C and 775°C resulted from re-oxidation of the catalyst after reduction. Also, MoO₃ phase observed at 720°C indicates that there is formation of oxide phases at lower temperatures.



Figure 4.3: XRD results for the prepared catalysts after reduction at different temperatures.

In addition, the increase in reduction temperatures used during the synthesis of MoFeP catalysts resulted in the continuous growth of MoFeP crystallites, as evidenced by the increase in average crystallites size from 26 nm at 720°C to 30 nm at 800°C estimated using the Scherrer equation in **Error! Reference source not found.** below. Furthermore, according to the trend observed in XRD experiments, the increase in reduction temperatures also led to the decrease in BET surface areas of the resulting MoFeP catalysts as determined by N₂ physisorption experiments as shown in Table 4.2 below.

| Catalyst | BET (m²/g)* | Average crystallite size(nm) |
|-------------|----------------|------------------------------------|
| R-MoFeP_720 | 5 | 26 |
| R-MoFeP_750 | 4 | 27 |
| R-MoFeP_775 | 3 | 28 |
| R-MoFeP_800 | 2 | 30 |

Table 4.2: Physical properties of MoFeP catalyst

*BET specific surface area calculated by BET; Average crystalline size calculated by Scherrer equation.

Therefore, the pure MoFeP phase was successfully developed at reduction temperature ranging from 720°C to 750°C based on XRD results obtained compared to the simulated results. The preparation method included the mixing of Mo, Fe and P precursors at 1:1:1 molar ratio by Pichini Method. Thereafter, calcination at 550°C for six hours followed by reduction. The pure phase at 750°C obtained was used for further synthesis of supported and promoted catalysts.



Figure 4.4: XRD of supported MoFeP catalysts (a)MoFeP/Al₂O₃ (b)MoFeP/SiO₂

XRD analysis of the supported MoFeP catalysts with 20 wt % active material all showed the same pattern as indicated in Figure 4.4. They both showed the phases of their respective supports and the MoFeP pure phase. This suggests that the active material is well dispersed on the surface. However, in MoFeP/SiO₂ catalyst, there is a small peak indicating Fe₅Si₃ phase which might be caused by interaction of Fe and Si at high reduction temperature.



Figure 4.5: XRD of Supported FePO₄ catalysts (a)FePO₄/Al₂O₃ (b)FePO₄/SiO₂

XRD analysis of the supported FePO₄ catalysts with 20 wt % active material showed a different pattern. By comparing the FePO₄/Al₂O₃ peak and Alumina peak it can be concluded that the FePO₄/Al₂O₃ peak came from the support. This suggests that the active material is well dispersed on the surface [57]. It also points towards small particles formed by the metal species [58]. On the other hand, dominant peak of FePO₄ could be detected in FePO₄ catalyst.



Figure 4.6: XRD of supported MoO₃ catalysts (a)MoO₃/Al₂O₃ (b)MoO₃/SiO₂

Unlike the phenomenon seen in FePO₄ based catalysts, all peaks of MoO_3 were detected in both supports, that is MoO_3/Al_2O_3 and MoO_3/SiO_2 as shown in Figure 4.4. This signifies that the MoO3 are large and well defined.



Figure 4.7: XRD for Ru-MoFeP/Al₂O₃ catalyst, prepared by1% loading of Ru on MoFeP/Al₂O₃ catalyst followed by calcination at 550°C with subsequent reduction at 750°C and finally passivation.

Ru-MoFeP/Al₂O₃ shown in Figure 4.7 above, is similar to the MoFeP/Al₂O₃ phase in Figure 4.4 (a) above. The is because the 1% of Ru added is well dispersed on the surface. This also explains the small particle size formed by Ru promoter. This is the similar case to Ru-MoFeP/SiO₂ catalyst as well.



Figure 4.8: High-angle annular dark-field scanning-STEM of Ru-MoFeP/SiO₂ catalyst.

Moreover, the morphology and the elemental mapping for Ru-MoFeP/SiO₂ was studied to illustrate the dispersion of the active phase on the support. Figure 4.8 shows the high-angle annular darkfield scanning transmission electron microscope (HAADF-TEM) for Ru-MoFeP/SiO₂ catalyst. It was observed that the active phase was homogenously dispersed on the support as hypothesized from XRD crystallite size analysis. The EDS elemental mapping of Mo, Fe, Ru and P as seen in Figure 4.8 indicated that the elements are well overlapped on each other suggesting the MoFeP formation. The Si and O mapping is originated from the support. The HAADF images for Ru-MoFeP/Al₂O₃ appeared to be similar, as shown in Figure 4.9 below. Therefore, it can be concluded that both silica and powdered gamma-alumina support provide high dispersion of active and promoted phase.



Figure 4.9: High-angle annular dark-field scanning-STEM of MoFeP/Al₂O₃ catalyst.

Catalyst synthesis was achieved using commercially produced powdered alumina support. The citric acid which induces homogenous active phase was impregnated sequentially onto the powder support. Herein, the diffusion of the promoted active phase was probed using SEM-EDS linear scan. The linear scan of 2.5µm Ru-MoFeP/SiO₂ is shown in Figure 4.10 (a and b). It is clearly seen that, Mo, Fe, P and Ru are evenly distributed along the surface of the particle based on the preparation ratios. However, Si and O elements show higher count which comes from the support.



Figure 4.10: Linear scan of powdered alumina supported Ru-MoFeP catalyst (2.5 μ m) (a-b) and MoFeP/Al₂O₃ (1 μ m) (c-d) using STEM-EDS elemental line mapping.

Additionally, another elemental linear scan for 20 wt% MoFeP/Al₂O₃ support was investigated, Figure 4.10 (c and d) above. The maximum scan (cps) distance observed for MoFeP/Al₂O₃ is about. 2000 um without large deviation of elemental counts. From the linear scan, it can be concluded that powdered alumina support has slightly better dispersion than the silica support.

4.2. Carbon based conversion

The analysis for conversions, product distribution and formation rates was done using raw data obtained from GC-MS and GC-FID. The raw data obtained is attached separately in the submission platform with a name "Raw Data".



Figure 4.11: Carbon based conversion of MoFeP catalyst. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.

This section will describe the disappearance of all feedstocks observed in the organic phase. The carbon-based conversion for all components was about 100% for MoFeP based catalysts except for phenol which increases from 5 to 52 and 73% for MoFeP, MoFeP/Al₂O₃ and Ru-MoFeP/Al₂O₃, respectively Figure 4.11. The good activity of C-O bond cleavage in oxygenate conversion on MoFeP is in good agreement with reported remarkable Caromatic-O bond cleavage activity of aryl ethers with high aromatic selectivity[3], phenol to benzene and cyclohexanol to cyclohexene on the bulk MoFeP catalysts [15]. In MoFeP, 1: 1 molar ratio of Mo: Fe caused a charge separation between metallic surface (MoFe) and P species. The charge separation gab between more oxophilic Mo and electronegative P could possibly create the required coordination environment for hydrodeoxygenation reactions due to either ensemble or ligand effects, thus enhance the Lewis acidity [59].



Figure 4.12: Carbon based conversion of MoO₃ and FePO₄ catalysts. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.

FePO₄ based catalyst showed 100% conversion in Acetic acid and Guaiacol only while MoO₃ showed 100% conversion in all components except phenol and Eugenol. The respective catalysts supported on Silica showed similar conversions with slightly more conversion in Alumina supported catalyst. FePO₄ catalyst showed the least amount of conversion of all the catalysts. The mechanism for the hydrodeoxygenation activity for the bulk bimetallic catalyst proposed based on DFT and time resolved experiment has all pointed to the role of Lewis acid character in reducing the activation energy [14, 60] required to cleave the C–O bond in the aromatic alcohol with higher phenolic bond energy (469 kJ/mol) [61]. The MoFeP has been identified as the main active phase for the hydrodeoxygenation reaction based on analysis of the activity of several crystalline phased from the FePO₄+MoO₃ precursors towards HDO reactions of phenolics compounds [3]. The activity of catalysts follows the order of Ru-MoFeP/Al₂O₃ > Ru-MoFeP/SiO₂ > MoO₃/Al₂O₃ > MoGeP/Al₂O₃ > MoFeP/SiO₂ > MoFeP/SiO₂ > MoFeP/Al₂O₃ > KePO₄/SiO₂. The supported catalyst shows an improved activity as compared to the bulk MoFeP catalyst due to large surface area and larger amount of exposed active sites. The increased in the conversion in Ru-MoFeP/Al₂O₃

and Ru-MoFeP/SiO₂ may be due to the hydrogenation ability of the Ru promoted catalyst towards hydrogen spillage. The mechanism of direct hydrodeoxygenation requires C-OH cleavage via hydrogenolysis [61].



4.3. Organic phase product distribution.

Figure 4.13: Organic phase distribution of the liquid product. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.

The product distribution was based on two lumped group, namely oxygen containing compounds (oxygenates) and hydrocarbons.In MoFeP based catalyst, the oxygenates decreased from 95% to 87% and finally to 23%, while hydrocarbon content increased from 5, to 23 and finally to 77 % selectivity from MoFeP, MoFeP/Al₂O₃ and Ru-MoFeP/Al₂O₃, respectively. However, In MoO₃ based catalyst, the hydrocarbon content increased from 8 to 13% selectively from MoO₃/SiO₂ and

MoO₃/Al₂O₃, respectively. While in FePO₄ based catalyst, minimum to no hydrocarbons were observed. It can be generally observed that there is a remarkable hydrodeoxygenation activity from the promoted catalyst as compared to the bulk and supported catalyst. The effects of the promoter can be further studied based on the detailed product analysis of the organic phase.

4.4. Organic phase product distribution.

The product distribution of bio-oil can be classified into four groups, namely light oxygenates such as acetone, ethanol, acetaldehyde, 2-butanone, furan and pentanone. These products originate form acetic acid, acetol and furfural hydrodeoxygenation reactions. Secondly, phenolics such as anisole and cresol, reaction intermediate products from guaiacol conversion to hydrocarbons [62-65]. These reaction intermediates were dominant mostly in supported catalysts. The next product spectrum was alkylated phenolics compounds. Finally, the last group of compounds are deoxygenated compounds (Zone IV) such as cyclohexene, propyl-cyclohexene, benzene, xylene isomers, C9 aromatics, naphthenes and 41aphthalene, benzofuran, alkylated phenols, phenolics compounds at the main products.

In MoFeP based catalyst, the bulk catalyst produces more light oxygenates compared to the supported and the promoted catalysts. On the other hand, MoFeP supported catalysts dominantly produce alkylated phenolics compared to bulk and promoted catalysts. As observed in Figure 4.14 below, the promoted catalyst led to formation of large fraction of aromatics. The formation rate (mol/gcat*s) was calculated based on net Carbon molar rate for each zone per the weight of active catalyst. Pure MoFeP catalyst has the lowest formation rates compared to its supported and promoted versions.



Figure 4.14: Formation rates of organic phase distribution of MoFeP based catalysts. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.

Figure 4.15 shows the formation rates of supported MoO₃ and FePO₄ based catalysts. They dominantly produce alkylated phenolics. However, MoO₃ catalyst shows more selectivity to alkylated aromatics compared to FePO₄ based catalysts. Overall, FePO₄ based catalyst has lower formation rate compared to all other catalysts tested. The formation rate follows the order Ru-MoFeP/Al₂O₃ > Ru-MoFeP/SiO₂ > MoO₃/Al₂O₃ > MoO₃/SiO₂ > MoFeP/Al₂O₃ > MoFeP/SiO₂ > MoFeP/SiO₂ > MoFeP/Al₂O₃ > FePO₄/Al₂O₃ > FePO₄/SiO₂ which is similar to the catalyst activity.



Figure 4.15: Formation rates of organic phase distribution of MoO₃ and FePO₄ based catalysts. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.

4.5. Product distribution and reaction pathway.

Reaction pathway can be proposed based on the detailed product distribution of the catalysts. The network can be considered as dependent via several intersecting pathways. The intra molecular reactions and intersection network between products and feedstock clearly explains the function of the catalysts.



Figure 4.16: Product distribution of bulk MoFeP catalyst. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.



Figure 4.17: Product distribution of MoFeP/Al₂O₃. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.



Figure 4.18: Product distribution of Ru-MoFeP/Al₂O₃. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.



Figure 4.19: Product distribution of MoO₃ based catalysts. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.



Figure 4.20: Product distribution of FePO₄ based catalysts. Reaction conditions: temperature: 400°C, total pressure: 20 bar, H₂ partial pressure: 14.7 bar, N₂: 1.5 bar, weight of catalyst: 4 g, feeding rate: 0.04 ml/min, total reaction time: 9 h, WHSV excluding water: 0.94 h-1.

Based on the detailed product distribution of catalysts as shown in Figure 4.16, Figure 4.17, Figure 4.18, Figure 4.19 and Figure 4.20, a reaction network is proposed for the conversion of the simulated feedstock to aromatics on catalyst bed.



Figure 4.21: Proposed reaction pathway based on observed products for 6-component tandem catalytic upgrading of simulated bio oil to biofuel [66]

When considering acetic-acid feed component, three pathways were observed, as shown in Figure 4.21 above, based on the final product analysis. Route (1) involves deprotonation-yielding acetate, which further decompose to yield methane and CO2 via decarboxylation pathway. The route (2) is the ketonization pathway via bimolecular coupling of acetic acid to produce acetone, CO2 and water via either bulk or surface mechanism. The formed acetone can further undergo aldol condensation to yield isophorone, a trimer [67, 68]. The isophorone can further dehydrate to an array of aromatics as observed [56, 69, 70]. Furthermore, under route (3), dehydration of acetic resulted in the formation of acetates, an acetyl which can be hydrogenated to acetaldehyde as observed in the products spectrum. Acetaldehyde further undergo hydrogenation to yield ethanol. The formed ethanol, and acetone from acetic acid are potential alkylation reactant. The acetic acid

reaction pathway observed here as reported by shown the production of ethanol via acetates formation or the production of acetone via ketonization pathway [71-76].

In addition, acetol could undergo two reaction routes (4 and 5), direct hydrogenation (route 5) to propylene glycol is favored at lower temperature, less than 200 oC. This product was not observed due to high temperature of 400°C [77]. Acetone formed can further undergo aldol condensation as described in Figure 4.21 above, not forgetting the possibility of self-coupling of acetol to cyclopentanone, which was also observed. The acetone, ethanol could be dehydrated to ethane and propene via hydrogenolysis.

Furthermore, furfural conversion pathway involves the decarbonylation (route 7) and hydrogenation (route 6) to yield CO, furan and furan alcohol, respectively. However, the formation of benzofuran suggest possible reaction between furan and phenol/benzene. In addition, the sequential hydrogenation of furan-alcohol resulted in the formation of the observed 2-pentanone. The light oxygenates obtained were mostly observed under MoFeP and MoO₃ based catalysts than supported MoFeP catalyst. Therefore, higher acidic functionality consumed these light oxygenates to other alkylated products.

Moreover, the conversion of phenol to hydrocarbons is one of the model compounds well studied in the literature due to the difficulty in breaking the aromatic alcohol bond [61]. The reaction route observed for phenol includes direct deoxygenation via hydrogenolysis pathway on the bimetallic surface. The observed cyclohexene yield of less than 5 % for Ru promoted catalyst, suggest less hydrogenation route as compared direct hydrodeoxygenation. Also, alkylated reaction involving ethanol (9) and acetone (10) with phenol yielded methyl and ethyl phenolics as observed predominantly in the supported catalyst.

Guaiacol is also another well studied model compound in literature for HDO activity due to the presence of hydroxy and methoxy functional group attached to the aromatic ring [66]. The possible reaction route are demethylation (route 10) and demethoxylation (route 11) yielding methane and methoxy that could be protonated to form methanol. The formation methanol was not observed however, methane was observed but methanol could be consumed via alkylation reaction. Possible isomerization reaction can lead to methyl phenol or dimethyl phenol that were significantly observed for the supported catalyst. The observed anisole and para-cresol under supported catalyst suggest possible hydroxy group elimination and later isomerization to yield toluene and xylene

isomers. Alkylation reaction between intermediates such as anisole, phenol and cresol gave several alkylated phenols on supported catalyst and further direct oxygen removal to hydrocarbons on Ru promoted catalyst.

Finaly, hydrodeoxygenation reaction route for eugenol is congruent to guaiacol and phenol. Eugenol is a guaiacol with 2-propene ring attached at para position. Therefore, the reactions observed in guaiacol were also observed similarly in using eugenol as feed. However, the formation of propyl-cyclohexane via hydrogenation of aromatic ring could be formed after hydrodeoxygenation reaction or the alkylation of acetone to phenolics could also lead to similar pathway based on the observed products.

In conclusion, the nature of the cascading and reactants, products and intermediate inter and intra interactions suggest that more modification and study of Ru-MoFeP/Al₂O₃ is needed to achieve higher degree of deoxygenation using realistic bio oil feed. However, a remarkable reduction in the catalytic hydrodeoxygenation activity for bulk MoFeP catalyst was observed due to the presence of the light oxygenates in the feedstock, while the supported catalyst promoted significantly alkylation and hydrodeoxygenation, respectively.

4.6. Reproducibility

The reproducibility of the results was tested by repeating the experiment using MoO_3/SiO_2 catalyst. During the experiment, same catalyst and the same conditions were used, and the results were compared to the initial experiment. The estimation of carbon balance for both experiments is tabulated in Table 4.3 below. The repeated experiment showed a slightly higher selectivity in gas that caused slight decrease in bio-oil yield.

| | MoO ₃ /SiO ₂ (EXP1) | MoO ₃ /SiO ₂ (EXP2) | |
|--|---|---|--|
| | (moles) | (moles) | |
| Total carbon in feed | 0.8319 | 0.8319 | |
| Total carbon in bio-oil(experimental) | 0.8068 | 0.7945 | |
| Gas analysis (experimental) | 0.008 | 0.010 | |
| Lost carbon (coke+spillage+exp errors) | 0.017 | 0.025 | |
| ERROR (%) | 2.03 | 3.03 | |

Table 4.3: Carbon balance of MoO₃/SiO₂, experiment 1 and 2



Figure 4.22: Carbon based conversion of reactants using MoO_3/SiO_2 catalyst in both experiments 1 and 2. Experiments were performed at 400°C, pH₂=20 bar, for 9 hours and flow of bio-oil was 0.04 ml/min.

In terms of conversion of the reactants, all acetic acid, acetol and guaiacol were also 100% converted in the repeated experiment. The phenol conversion is very similar for both experiments, while the furfural and eugenol conversions were slightly higher in experiment 1 and experiment 2 respectively.

4.7. Carbon Balance

Due to lack of appropriate method for quantification of coke for all the used catalyst, coke analysis could not be included. However, the carbon balance error in all experiments was below 5% and therefore formation of coke could be assumed to be minimal. Furthermore, during the end of the experiment after dismantling the reactor, some clogging in the bio-oil feeding tube was noticed and this could potentially result to lost in carbon by clog formation. Liquid sampling was done by collecting a small amount of liquid sample and it was analyzed t assume the representative of the oil phase. To clean the reactor for the next experiment, all carbon was extracted from the condenser with acetone, but the total amount of carbon resulting from the cleaning process was not quantified. Because of this, the carbon balance is not complete if the mass of liquid for the initial sample is used in quantification calculations. Carbon balance for all the activity experiments is shown in table below.

| Catalyst | Total carbon in | Total carbon in bio-oil | gas analysis (experimental) | Lost carbon | Error [%] |
|---|--------------------|----------------------------|--------------------------------|----------------|--------------|
| | [Cmole] | (experimental) | [Cmole] | [Cmole] | |
| MoFeP | 1.1090 | 1.065 | 0.008 | 0.036 | 3.28 |
| MoO ₃ /Al ₂ O ₃ | 0.8319 | 0.8068 | 0.008 | 0.017 | 2.03 |
| MoO ₃ /SiO ₂ | 0.8319 | 0.7893 | 0.004 | 0.038 | 4.61 |
| FePO ₄ /Al ₂ O ₃ | 0.8319 | 0.7820 | 0.010 | 0.040 | 4.75 |
| FePO ₄ /SiO ₂ | 0.8319 | 0.7918 | 0.004 | 0.036 | 4.32 |
| MoFeP/Al ₂ O ₃ | 0.8319 | 0.7873 | 0.012 | 0.032 | 3.91 |
| MoFeP/SiO ₂ | 0.8319 | 0.7977 | 0.012 | 0.022 | 2.66 |
| Ru-MoFeP/Al ₂ O ₃ | 0.8319 | 0.8144 | 0.012 | 0.005 | 0.64 |
| Ru-MoFeP/SiO ₂ | 0.8319 | 0.7945 | 0.012 | 0.009 | 1.03 |

Table 4.4: Carbon balance for activity measurements

The highest error observed is for the FePO₄ based catalyst while the lowest error was obtained for the Ru-promoted catalysts. Despite obtaining experimental errors less than 5%, more work should be done to investigate and analyze the carbon loss. Neglecting some peaks from GC-MS might also account to some of the errors during the analysis.

5. Conclusion

The pure phase of MoFeP was successfully formed at a reduction temperature between 725°C and 750°C. The phases were confirmed by XRD results as well as EDX. The phases for MoFeP could still be detected in the supported and promoted phases, showing consistency of the pure phase. Although both supports have shown similar testing experimental results, powdered alumina exhibits slightly better dispersion of the active phase. Therefore, this explains why alumina supported catalyst show slightly better activity compared to silica supported equivalents.

A 100 % conversion of furfural, acetol and acetic acid, >90% conversion of guaiacol and >90% eugenol was obtained for all catalysts, except FePO₄ based catalysts. Ru-promoted MoFeP based catalysts showed the highest conversion of phenol to over 70%. The phenol conversion for the other catalysts ranged about 10% for MoFeP and FePO₄ based catalysts and 50% for both MoFeP-supported catalysts and MoO₃ based catalysts. The main products were in the liquid phase, which contained light oxygenates, phenolics, alkylated phenolics and alkylated aromatics. Deoxygenation and hydrocracking are the proposed reactions happening for acetic acid and acetol. They mainly yielded hydrocarbons going to gas phase or acting as alkylating agents. Alkylation and deoxygenation were suggested dominating for phenol, guaiacol and iso-eugenol upgrading. Furfural products might have resulted from ring rearrangement, deoxygenation or combinations with benzene.

Overall, the synthesis, characterization and application of MoFeP based, MoO₃ based and FePO₄ based catalysts have been studied for application under industrially relevant conditions. The Ru cluster promoted catalyst showed remarkable selectivity to C-O phenolic bonds cleavage towards high yield of biofuel production using simulated bio-oil feedstock. A significant hydrodeoxygenation degree was observed for the Ru-promoted catalyst as compared to bulk and supported MoFeP catalyst. The detailed analysis of the product suggests sequence reactions such as ketonization, dehydration and aldol condensation occurring under upstream catalyst, while alkylation and hydrodeoxygenation happens under the downstream bed. The final product spectrum

clearly indicates the production of blended jet-fuel range aromatics (C_{7+}) from simulated bio-oil. Therefore, a much realistic approach towards biomass to bio-oil to biofuel cascading steps towards renewable inclusion into the aviation-fuel mix has been established using tandem catalytic strategy.

6. Suggestions for further work

Suggestions for further work are listed below:

- The rig must be further modified to reduce clogging effect occurring in the feeding tube.
- Installation of liquid sampling device to ensure accurate amount of biofuel is collected and can later be analyzed.
- Quantify the feed by the effective carbon method to verify the numbers in this project.
- Redo calibration of GC-TCD to include all the detected peaks in the quantification. of the gas phase.
- Testing the catalysts with individual components in the simulated bio-oil to confirm the results obtained in this project.
- Test activity with only support to see what reactions are catalyzed by the support.
- Try out other bimetallic phosphate catalysts using cheaper metals like Nikel.
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Appendix

Appendix A: List of chemicals

Table A: List of chemicals used in this project

| Chemical | Purity | State | Purpose | Supplier |
|------------------|--------|-------|-----------|---------------|
| (NH4)6M07O24*H2O | 99% | S | Precursor | Sigma Aldrich |
| Fe(NO3)2*9H2O | 99.99% | S | Precursor | Sigma Aldrich |
| NH4H2PO4 | 99.5% | S | Precursor | Sigma Aldrich |

Appendix B: XRD-Chromatograms



Figure 1B: XRD for MoO₃



Figure 2B: XRD for calcined MoFeP



Figure 3B: XRD for FePO₄



Figure 4B: XRD for reduced MoFeP_750

Appendix C: Crystalline size calculations using DIFFRAC.EVA software.



Figure C: Estimated crystalline size of MoFeP_720 using DIFFRAC.EVA software.

Appendix D: Catalyst synthesis

The catalyst was prepared based on calculations as summarized in the attached excel figure:

| Citric acid was ideal for dissolving | g these | | | | Precursor | used | Molar mass(g/mol) | Element | Molar mass |
|--------------------------------------|-------------|--------------|--------------|--------|------------------------------------|---|-------------------|---------|------------|
| precursors due to its ability to lig | ate the m | etals and in | hibit precip | oitate | 1. (NH ₄) ₆ | Mo ₇ O ₂₄ 4H ₂ O | 1235.86 | Mo | 95.95 |
| formation | | | | | 2. (NH ₄)H | ₂ PO ₄ | 132.06 | Р | 30.97376 |
| Citric acid molar mass = | 192.124 | g/mol | | | 3. Fe(NO ₃ |)₃.9H2O | 404 | Fe | 55.845 |
| Citric acid concentration used = | 1 | м | | | | | | | |
| Required molar ratio of citric acid | d to salts | = 2:1 | 0.666667 | | | | | | |
| Required volume of citric acid | 75 | ml | | | | | | | |
| Moles of Citric Acid | 0.075 | moles | | | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| 1. MoP | | | | | | | | | |
| Mole ratio required: Citric acid : | Mo : P = | 4 | 1 | 1 | Ratio sum | 6 | | | |
| Grams of Citric acid = | | 14.4093 | g | | | | | | |
| Grams of Mo precursor required | = | 3.310339 | g | | | | | | |
| Grams of P precursor required = | | 2.476125 | g | | | | | | |
| | | | | | | | | | |
| 2. FeP | | | | | | | | | |
| Mole ratio required = Citric acid : | : Mo : Fe = | 4 | 1 | 1 | Ratio sum | 6 | | | |
| Grams of Citric acid = | | 14.4093 | g | | | | | | |
| Grams of Fe precursor required = | = | 7.575 | g | | | | | | |
| Grams of P precursor required = | | 2.476125 | g | | | | | | |
| | | | | | | | | | |
| 3. MoFeP | | | | | | | | | |
| Mole ratio required=Citric acid:N | lo:Fe:P = | 6 | 1 | 1 | 1 Ratio sum | 9 | | | |
| Grams of Citric acid = | | 14.4093 | g | | | | | | |
| Grams of Mo precursor required | = | 2.206893 | g | | | | | | |
| Grams of Fe precursor required = | - | 5.05 | g | | | | | | |
| Grams of P precursor required = | | 1.65075 | g | | | | | | |

Figure D: Excel sheet showing all computations done during catalyst preparation by Pechini Method

Appendix E: Simulated Bio-oil Synthesis

| Mass composition of s | simulated | bio-oil(g |) | | Density(| ;/ml) | Volume(ml) | Percenta | ge compositio | n in volume(%) |
|-------------------------|-----------|-----------|------------|-------------|-----------|-------------|-------------|----------|---------------|----------------|
| 1. Distilled Water | 28.7 | | | | 1 | | 28.7 | | 29.07 | |
| 2. Acetic acid | 12.3 | | | | 1.049 | | 11.72545 | | 11.88 | |
| 3. Acetol | 13.8 | | | | 0.831 | | 16.6065 | | 16.82 | |
| 4. Furfural | 10.6 | | | | 1.1598 | | 9.139507 | | 9.26 | |
| 5. Phenol | 15.7 | | | | 1.07 | | 14.6729 | | 14.86 | |
| 6. Guaiacol | 9.1 | | | | 1.129 | | 8.06023 | | 8.17 | |
| 7. Eugenol | 10.4 | | | | 1.06 | | 9.811321 | | 9.94 | |
| Total mass | 100.6 | | | | | Total vol. | 98.71591 | | | |
| Reaction conditions | | | | | | | | | | |
| 1. Feeding rate | 0.04 | ml/min | | | | | | | | |
| 2. Reaction time | 12 | h | | | | | | | | |
| Total volume required | 28.8 | ml | | | | | | | | |
| Simulated Bio-oil synth | nesis | | | | | | | | | |
| Volume to synthesize | 150 | ml | (Insert th | e amount of | liquid yo | u want to s | synthesize) | | | |
| | | | | | | | | | | |
| Components to mix | | | | | | | | | | |
| 1. Distilled Water | 43.61 | ml | | | | | | | | |
| 2. Acetic Acid | 17.82 | ml | | | | | | | | |
| 3. Acetol | 25.23 | ml | | | | | | | | |
| 4. Furfural | 13.89 | ml | | | | | | | | |
| 5. Phenol | 22.30 | ml | | | | | | | | |
| 6. Guaiacol | 12.25 | ml | | | | | | | | |
| 7. Eugenol | 14.91 | ml | | | | | | | | |

Figure E: Excel sheet showing all computations done during preparation of simulated bio-oil.

Appendix F: Risk Assessment

| ID | 40078 | Status | Date |
|-------------|--|--------------------|------------|
| Risk Area | Risikovurdering: Helse, miljø og sikkerhet (HMS) | Created | 16.09.2020 |
| Created by | Leo Gosbert Mboyerwa | Assessment started | 17.09.2020 |
| Responsible | Leo Gosbert Mboyerwa | Measures decided | |
| | | Closed | |

Risk Assessment: CAT, Master student, 2021, Leo Gosbert Mboyerwa

Valid from-to date:

9/16/2020 - 9/16/2023

Location:

IKP, Kjemiblokk 5, Gløshaugen Campus, Hall D

Goal / purpose

Synthesis and characterization of the Ru promoted MoFe phosphide catalyst supported on γ-alumina which is used for hydrodeoxygenation reaction in the bio-oil up-gradation process. The main goal is to increase yield and improve the quality of produced bio-oil.

The performance of the catalyst will be tested using Rig 2.11(a) where simulated bio-oil is as the feed. The simulated bio-oil will be synthesized using various chemicals.

Background

Decomposition of lignocellulose biomass result into bio-oil which contains aromatic compounds mostly originated from lignin. Furthermore, the oil also contains oxygenates of C1-C6 carbon length, such as acetic acid, acetol, anhydrous-sugar, furan, alcohol and carbonyls like ketone and aldehyde, which originate from cellulose and hemicellulose components. These components result in overall high oxygen content of pyrolysis oil leading to high acidity, increased viscosity and phase separation of the oil. On top of that, high oxygen and water content of pyrolysis oil compared to fossil fuel results in lower heating values (15–19 MJ/kg) compared to fossil fuels (40 MJ/kg). Lignin has become an attractive source of gasoline-range hydrocarbons due to its large aromatic content and oxygen to carbon ratio compared to cellulose and hemicellulose. Nevertheless, this has been limiting because of the high amount of aryl ethers and phenolic compounds present in bio-oils produced from lignocellulosic biomass. To remove oxygen from bio-oil, catalytic hydrodeoxygenation is required. The phenolic C–O bond energy is large (468 kJ/mol) and makes the direct hydrodeoxygenation difficult. It, therefore, requires several conditions which favour C-O bond cleavage resulting in selectivity towards the production of aromatic compounds

Description and limitations

MATERIAL USED FOR CATALYST AND SIMULATED BIO-OIL SYNTHESIS: FOR CATALYST:

1. Ammonium phosphate dibasic ((NH4)2HPO4, Sigma Aldrich, 99%,

- 2. Iron nitrate nonahydrate (FeNO3·9H2O, Sigma Aldrich, 99%),
- 3. Ammonium molybdate tetrahydrate ((NH4)6Mo7O24.4H2O, Sigma Aldrich, 99%),
- 3. RuCl3 (Sigma Aldrich, 99%),

4. Citric acid (Sigma Aldrich, 99 %),

5. Sasol chemicals USA, LLC, Catalox ® alumina spheres (surface area: 109.8 m2/g, size: 4-5.5 mm).

FOR SIMULATED BIO-OIL: all with purity >99 %.

- 6. Acetic acid,
- 7. Acetol,
- 8. Furfural,
- 9. Phenol,
- 10. Guaiacol
- 11. Eugenol

PREPARATION OF (Ru-MoFeP/Al2O3) CATALYST :

1. MoFeP/Al2O3 will be prepared by a modified Pichini method using the sequential wetness impregnation method.

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2. Ru is then impregnated onto the calcined catalyst (MoFeP/Al2O3) using the incipient wetness impregnation method.

3. The Ru promoted catalyst on MoFeP/Al2O3 will be subsequently dried 100C (4 h) and calcined at 500C using 1C/min heating rate, dwell time at final temperature is 5 h.

4. The active phase, Ru-MoFeP, will be obtained using a temperature reduction method at a heating rate of 1 C/min at 250 and 700C to react all phosphorus and reduced oxides to metallic form 51, 102, 107 in the presence of 75% H2 in Nitrogen.

NOTE: More procedures will be updated as I progress.

CHARACTERIZATION TECHNIQUES USED:

1. BET - Specific surface area.

2. XRF - Chemisorption

- 3. XRD Crystallinity
- 4. S(T)EM Surface Morphology

5. FTIR, GC-MS, GC-FID - Chemical characterization of bio-oil

RIG OPERATION:

Rig 2.11(a) will be used. Only one reactor will be included (hydrogen is utilized for this experiment).

The reactor will be used for upgradation ((1 atm and 300 to 500C)) in a hydrogen atmosphere. Initial runs will be run on carboncarbon coupling catalyst then hydro-deoxygenation (HDO)catalyst. later both the catalyst will be combined in the dual bed configuration.

OPERATING PROCEDURES:

Weigh the catalyst and heat to the final temperature in the reactor.

1. Get the ice from K4 for the condensing

2. Fit the condenser to the setup after adding 3ml of cyclohexane in it. Ice surrounds the condenser to increase the condensation rate.

3. Set the required nitrogen and hydrogen flow as per requirement. (only nitrogen will be used for preheating to set final temperature, hydrogen will be used only when in-situ reduction of the catalyst is required)

4. Connect the gasbag to the condenser and start the timer as soon as you open the nozzle of the gasbag.

5. Close the nozzle and disconnect the airbag after the allocated time.

6. Shut down the reactor to cool down. (also unplug it to make sure the reactor doesn't have the power supply in order to avoid unnecessary heating in case the thermocouple is out of the reactor unknowingly).

ANALYSIS OF LIQUID AND GAS PRODUCTS:

A) GC for gas products in gasbag:

(Method: The gas is sent via a gas sampling valve by pressing the gas bag. The inlet valve is kept at 200 °C. The oven is initially kept at 45 °C for 6 min. The first heating ramp is 75 °C/min up to 190 °C and staying for 2 min. The second heating ramp is at 75 °C/min down to 45 °C/min. The FID (front detector) and TCD (back detector) detector is kept at 250 °C and 230 °C respectively. The contribution of each gas component is based on the internal standard calibration of their respective chemical gas)

- 1. Two runs in the GC are required.
- 2. Before running the analysis, I have to make sure that the H2 flow and airflow is ON.
- 3. After that when the system is ready, I have to press the bag in 15 sec.
- 4. it will take approximately 15 min to run 1 experiment.
- 5. Similarly I will do the 2nd run after 15 min.
- 6. I will analyze both the data and save it in a folder.
- 7. After doing both runs, I will close the H2 flow and airflow.

B) GC-MS and GC-FID for liquid product analysis:

(Method is common for both GC-MS and GC-FID: Oven temp: 40C, first ramp at 4C/min up to 150 and stay for 5min, 2nd ramp at 10C/min up to 270 and stay for 5min, split ratio: 200:1)

1. I will take the condenser out and pour the products in a small vial.

2. Then place the vial in the apparatus and after entering all required data in GC-MS online application, It will run for approximately 33min.

3. I will analyze and print the data.

C) Bio-oil will also be analyzed by FTIR to qualitatively analyze the functional groups. Operating FTIR is fairly simple, method: 32 scans or 64 scans at a resolution of 1 cm - 1, The spectral ranges from 7,500 - 370 cm - 1.

SWITCH OFF PROCEDURE:

1. When the reactor has cooled down, It will be removed and weighed in order to determine the coke formation.

- 2. The metal caps will then be removed in order to determine the amount of feedstock converted.
- 3. Then the condenser, gasbag, and the reactor will be cleaned by distilled water.
- 4. Spent catalysts will also be collected from the reactor and kept in a small vial and labelled precisely.
- 5. The cleaned parts of the reactor will later be placed in an oven to dry.

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6. Gasbag will be flushed with nitrogen and emptied for the next run. After flushing, it will be kept on the desk adjacent to the rig

2.10.

7. I will clean the reactor and other parts and place them in the oven before the next experiment.

Prerequesites, assumptions and simplifications

Safety measures related to spreading of COVID-19 infection:

• Will avoid touching face while working in the lab

• Disinfection before and after with ethanol on all surfaces that I'll be in contact with (doorknob – card reader with code panel. This would also apply to laboratory PC screen, keyboard, mouse, desk, and the label printing machine.

- Will ensure 2m distance from colleagues
- · Usage of nitrile gloves when touching shared lab set-ups and equipment
- Washing hands as often as possible'

The work assumes that proper training is given prior to the use of laboratories and equipment/instruments, to minimize the probability of user-caused mistakes. Safe storage and handling of samples between labs are crucial. The use of personal protective equipment are mandatory.

Also due to the current COVID pandemic, extra measures have been implemented in the labs to avoid propagation of the illness

Attachments

iron nitrate nonanhydrate.pdf RuCl3.pdf Ammonium phosphate dibasic.pdf Citric acid.pdf ammonium molybdate tetrahydrate.pdf Eugenol.pdf Guaiacol.pdf Acetic Acid.pdf Phenol.pdf Furfural.pdf Oxygen.pdf Nitrogen.pdf hydrogen.pdf apparatus card for rig 2.11(a).doc 2.11(a) rig procedure and risk assement.docx Boric acid.pdf Rig 2.11(a) PID(mod3).pdf

References

[Ingen registreringer]

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Summary, result and final evaluation

The summary presents an overview of hazards and incidents, in addition to risk result for each consequence area.

| Hazard: | Chemical handling and spillage | | | |
|-------------------|---|--|--|---|
| Incident: | Citric acid spills | | | |
| Consequence area: | Helse | Risk before measures: | Risiko after measures: | 0 |
| Incident: | Iron nitrate nanohydrate | | | |
| Consequence area: | Helse | Risk before measures: | Risiko after measures: | 0 |
| Hazard: | Gas leaks | | | |
| Incident: | Gas leakage through pipes, valves and fit | ting. | | |
| Consequence area: | Helse Ytre miljø | Risk before measures: Risk before measures: | Risiko after measures: Risiko after measures: | 0 |
| Hazard: | Working with X-Ray Equipment. | | | |
| Incident: | Exposure of X-RAYS from characterization | n equipment. | | |
| Consequence area: | Helse | Risk before measures: | Risiko after measures: | 0 |
| Hazard: | Using Boric Acid | | | |
| Incident: | Skin, eye and inhalation of Boric acid duri | ng sample preparati | on. | |
| Consequence area: | Helse | Risk before measures: | Risiko after measures: | • |

| Hazard: | Using high pressure pressing machine. | | | | | |
|-------------------|---|---|---------------------------|------------|--|--|
| Incident: | Fracture of metallic sample holder under | Fracture of metallic sample holder under high pressure. | | | | |
| Consequence area: | Helse | Risk before measures: | Risiko after measures: | 0 | | |
| Hazard: | Handling of liquids during collection afte | r experiments | | | | |
| Incident: | Spill of liquid while collecting through GC vials | | | | | |
| Consequence area: | Helse | Risk before measures: | Risiko after measures: | 0 | | |
| Hazard: | High temperature operations | | | | | |
| Incident: | Risk when removing some components f | rom the rig. | | | | |
| Consequence area: | Helse | Risk before measures: | Risiko after measures: | \bigcirc | | |

Final evaluation

Organizational units and people involved

A risk assessment may apply to one or more organizational units, and involve several people. These are lsited below.

Organizational units which this risk assessment applies to

- Institutt for kjemisk prosessteknologi

Participants

De Chen Kumar Ranjan Rout Petter Tingelstad Kishore Rajendran Estelle Marie M. Vanhaecke Karin Wiggen Dragsten Anne Hoff Karthikai Selvan Sivasamy

Readers

-- -

[Ingen registreringer]

Others involved/stakeholders

[Ingen registreringer]

The following accept criteria have been decided for the risk area Risikovurdering: Helse, miljø og sikkerhet (HMS):

| Heise | |
|-------|--|
| | |
| | |
| | |



Materielle verdier



Omdømme



Ytre miljø

Overview of existing relevant measures which have been taken into account

The table below presents existing measures which have been take into account when assessing the likelihood and consequence of relevant incidents.

| Hazard | Incident | Measures taken into account |
|---|---|---|
| Chemical handling and spillage | Citric acid spills | Personal Measures |
| | Citric acid spills | Material safety and data sheets (MSMDs) |
| | Iron nitrate nanohydrate | Personal Measures |
| | Iron nitrate nanohydrate | Material safety and data sheets (MSMDs) |
| Gas leaks | Gas leakage through pipes, valves and fitting. | Personal Measures |
| | Gas leakage through pipes, valves and fitting. | Material safety and data sheets (MSMDs) |
| | Gas leakage through pipes, valves and fitting. | Leak detection systems |
| | Gas leakage through pipes, valves and fitting. | Gas detectors and Alarm systems |
| Working with X-Ray Equipment. | Exposure of X-RAYS from characterization equipment. | Personal Measures |
| | Exposure of X-RAYS from characterization equipment. | Material safety and data sheets (MSMDs) |
| | Exposure of X-RAYS from characterization equipment. | Work alone alarm |
| | Exposure of X-RAYS from characterization equipment. | Instrument training |
| Using Boric Acid | Skin, eye and inhalation of Boric acid during sample preparation. | Personal Measures |
| | Skin, eye and inhalation of Boric acid during sample preparation. | Material safety and data sheets (MSMDs) |
| | Skin, eye and inhalation of Boric acid during sample preparation. | Work alone alarm |
| | Skin, eye and inhalation of Boric acid during sample preparation. | Instrument training |
| | Skin, eye and inhalation of Boric acid during sample preparation. | Use of Fume Hood |
| | Skin, eye and inhalation of Boric acid during sample preparation. | Fume Hoods |
| | Skin, eye and inhalation of Boric acid during sample preparation. | Fume Hoods |
| Using high pressure pressing machine. | Fracture of metallic sample holder under high pressure. | Personal Measures |
| | Fracture of metallic sample holder under high pressure. | Material safety and data sheets (MSMDs) |
| | Fracture of metallic sample holder under high pressure. | Work alone alarm |
| | Fracture of metallic sample holder under high pressure. | Instrument training |
| Handling of liquids during collection after experiments | Spill of liquid while collecting through GC vials | Personal Measures |
| High temperature operations | Risk when removing some components from the rig. | Personal Measures |

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| High temperature operations | Risk when removing some components | Instrument training | |
|-----------------------------|------------------------------------|---------------------|--|
| | from the rig. | | |

Existing relevant measures with descriptions:

Personal Measures

The use of personal protective equipment such as Safety goggles (mandatory in all laboratories), lab coat, Gloves, Gasmask, Filter mask, safety shoes, earplugs, etc.

Material safety and data sheets (MSMDs)

A Material Safety Data Sheet (MSDS) is a document that contains information on the potential hazards (health, fire, reactivity, and environmental) and how to work safely with the chemical product.

Leak detection systems

Leak detection is a control method used to identify, monitor, and measure the unintentional entry or escape of fluids and gases, usually from pressurized systems or into empty enclosures.

Gas detectors and Alarm systems

It is a system that detects the presence of gases in an area as part of a safety system. In our KinCat lab, the alarm indicated blue for low detection and red for high detection.

Work alone alarm

For emergency help especially when someone is working alone in the lab.

Instrument training

Characterization of Catalysts will require the use of various characterization instruments. The training of the use of these instruments will ensure the safe use of them.

Use of Fume Hood

Enables us to handle well chemicals that produce toxic fumes.

Fume Hoods

Fume hoods are used when the samples emit poisonous gases or fragments. They mostly prevent a person who is working with the samples from inhaling the samples.

Risk analysis with evaluation of likelihood and consequence

This part of the report presents detailed documentation of hazards, incidents and causes which have been evaluated. A summary of hazards and associated incidents is listed at the beginning.

The following hazards and incidents has been evaluated in this risk assessment:

Chemical handling and spillage

- Citric acid spills
- Iron nitrate nanohydrate
- Gas leaks
 - Gas leakage through pipes, valves and fitting.
- Working with X-Ray Equipment.
 - Exposure of X-RAYS from characterization equipment.
- Using Boric Acid
 - Skin, eye and inhalation of Boric acid during sample preparation.
- Using high pressure pressing machine.
 - Fracture of metallic sample holder under high pressure.
- Handling of liquids during collection after experiments
 - Spill of liquid while collecting through GC vials
- High temperature operations
 - Risk when removing some components from the rig.

Detailed view of hazards and incidents:

Hazard: Chemical handling and spillage

Spillage might occur during the preparation of catalyst and simulated bio-oil.

Incident: Citric acid spills

Likelihood of the incident (common to all consequence areas):

Kommentar:

P264 Wash skin thoroughly after handling.
P280 Wear eye protection/ face protection.
P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes.
Remove contact lenses, if present, and easy to do. Continue rinsing.
P337 + P313 If eye irritation persists: Get medical advice/ attention.

Consequence area: Helse

Assessed consequence: Very large (4)

Comment: skin irritation, therefore it is advisable to use gloves, lab coats, and goggles during handling. In case of exposure, wash the area several times with water, if irritation still persists, get medical attention.

.....

Less likely (2)

Incident: Iron nitrate nanohydrate

Likelihood of the incident (common to all consequence areas): Less likely (2)

Kommentar:

P280 Wear protective gloves/ protective clothing/ eye protection/ face protection.
P303 + P361 + P353 IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower.
P304 + P340 + P310 IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/doctor.
P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present, and easy to do. Continue rinsing.

Consequence area: Helse

Assessed consequence: Very large (4)

Comment: Hazard: H314 Causes severe skin burns and eye damage.

Risk:



Risk:



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Hazard: Gas leaks

Gas leakage might occur when performing experiment involving the rig.

Incident: Gas leakage through pipes, valves and fitting.

Rig operation involves the use of pressurized gases like hydrogen and nitrogen. Gas leaks usually occur through valves.

Likelihood of the incident (common to all consequence areas): Less likely (2)

Kommentar:

1. Human error during closing and opening of the valve. The valve might be left open unintentionally after the experiment.

2.Detectors are available inside the rig as well as in the hall. possible measures have been informed to us either to evacuate the room or to shut down the experiment based on the type of alarm.

Consequence area: Helse

Assessed consequence: Very large (4)

Comment: NH3:

H280 - CONTAINS GAS UNDER PRESSURE; MAY EXPLODE IF HEATED H314 - CAUSES SEVERE SKIN BURNS AND EYE DAMAGE H332 - HARMFUL IF INHALED

Carbon monoxide:

Hazard statements (CLP) : H220 - Extremely flammable gas.
H280 - Contains gas under pressure; may explode if heated.
H331 - Toxic if inhaled..
H360D - May damage the unborn child..
H372 - Causes damage to organs through prolonged or repeated exposure.

Carbon dioxide:

Hazard statements: H280 - CONTAINS GAS UNDER PRESSURE; MAY EXPLODE IF HEATED OSHA-H01 - MAY DISPLACE OXYGEN AND CAUSE RAPID SUFFOCATION CGA-HG01 - MAY CAUSE FROSTBITE CGA-HG03 - MAY INCREASE RESPIRATION AND HEART RATE

Consequence area: Ytre miljø

Assessed consequence: Very large (4)

Comment: Carbon dioxide:

Hazard statements: H280 - CONTAINS GAS UNDER PRESSURE; MAY EXPLODE IF HEATED



Risk:



Hazard: Working with X-Ray Equipment.

The use of equipment such as XRD and XRF for characterization of samples.

Incident: Exposure of X-RAYS from characterization equipment.

XRF and XRD contain X-rays. A person can be exposed if he or she does not operate the equipment appropriately.

Likelihood of the incident (common to all consequence areas): Unlikely (1)

Kommentar:

- 1. All advice of the Radiation Protection Advisor (RPA) is followed.
- 2. Interlocked enclosures should are provided.
- 3. Fail-safe warning devices are fitted.
- 5. Calibration of radiation monitor is tested.

Consequence area: Helse

Assessed consequence: Very large (4)

Comment: Without control measures or the operational procedures, X-rays represent an intolerable risk (likely, extremely harmful) under guidance given in BS 8800.



Risk:

Hazard: Using Boric Acid

Boric Acid is used during sample preparation when using XRF.

Incident: Skin, eye and inhalation of Boric acid during sample preparation.

Boric acid powder may get into contact with the skin, eyes or air pathways during sample preparation in the XRF lab.

Likelihood of the incident (common to all consequence areas): Less likely (2)

Kommentar:

or gas.

- 1. Use personal protective equipment. Avoid dust formation. Avoid breathing vapours, mist
- 2. Ensure adequate ventilation. Evacuate personnel to safe areas. Avoid breathing dust.
- 3. Prevent further leakage or spillage if safe to do so. Do not let product enter drains.
- 4. Pick up and arrange disposal without creating dust. Sweep up and shovel.
- 5. Keep in suitable, closed containers for disposal.

Consequence area: Helse

Assessed consequence: Very large (4)

Comment: 1. H360FD May damage fertility. May damage the unborn child.

2. P201 Obtain special instructions before use. P308 + P313 IF exposed or concerned: Get medical advice/ attention.

3. This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

Risk:



Page:

Hazard: Using high pressure pressing machine.

Pressing machine is used during sample preparation before using the XRF machine.

Incident: Fracture of metallic sample holder under high pressure.

When the pressure is over the calibrated limit, the metal sample holder may fracture and fly in jagged pieces.

Likelihood of the incident (common to all consequence areas): Less likely (2)

Kommentar:

- 1. An automatic locking in the case of unexpected pressure release or power failure.
- 2. Limited range of pressure in the device.
- 3. Simple design allows for lower risk and less room for mechanical error.

Consequence area: Helse

Assessed consequence: Large (3)

Comment: Under severe conditions, an operator can suffer lacerations and puncture wounds from sharp metal and other projectiles.

Risk:



Hazard: Handling of liquids during collection after experiments

The liquid products consist of aldehyde, ketone, acids, mono and polyaromatics. The total liquid weight collected will be less than a gram.

Incident: Spill of liquid while collecting through GC vials

The liquid products consist of aldehyde, ketone, acids, mono and polyaromatics. The components may cause potential hazards on the skin.

Likelihood of the incident (common to all consequence areas): Less likely (2)

Kommentar:

Hand gloves and protective goggles will be worn during the experiments which will help protect against spills. However, some hand gloves might be susceptible to corrosion and increase the chance of an incident.

Consequence area: Helse

Assessed consequence: Medium (2)

Comment: Hazard statement(s) H319 Causes serious eye irritation. Precautionary statement(s) P264 Wash skin thoroughly after handling. P280 Wear eye protection/ face protection. P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.



Hazard: High temperature operations

Experiments will be run at temperatures around 300 - 500 degrees centigrade.

Incident: Risk when removing some components from the rig.

After the experiment, some components are to be removed for cleaning or weighing. It is important to be careful.

Likelihood of the incident (common to all consequence areas): Less likely (2)

Kommentar:

Instrument training and instrumentation installed at the rig enables one to identify the temperature to the components. The component will only be removed when it cools down to room temperature.

Consequence area: Helse

Assessed consequence: Large (3)

Comment: This will lead to burns and wounds on the skin.



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Overview of risk mitiating measures which have been decided:

Below is an overview of risk mitigating measures, which are intended to contribute towards minimizing the likelihood and/or consequence of incidents:

Overview of risk mitigating measures which have been decided, with description:

Detailed view of assessed risk for each hazard/incident before and after mitigating measures



