Catalytic Conversion of Biomass for the Production of Hydrogen; Decomposition of Formic Acid

by

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science and Engineering
Department of Chemical Engineering
University of Toronto

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Abstract

Highly active bimetallic catalysts were synthesized and used for the decomposition of formic acid for the production of hydrogen. Ruthenium alloys were prepared and resulted in a maximum formic acid conversion of 68% (after one hour at 180 °C) and a turnover frequency of 0.7 s⁻¹ (at 5 wt% formic acid). The most promising catalysts were characterized by the means of X-ray diffraction and scanning electron microscopy. Kinetic studies were also carried out over these catalysts for the determination of reaction rate and turnover frequency. Promotion of Ru/C with tin, barium and cesium increased the formic acid conversion by 55%, 18% and 11% respectively.
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Chapter 1
Introduction

1 Introduction

1.1 Background

Dependence and reliance on renewable energy sources has been increasing during the past decade due to less availability of oil and global recognition of the current state of the environment caused by the injurious use of fossil fuels. The shift towards green energy production and consumption has been observed in different parts of the world, especially in developed countries, as a result of either participation in national and international protocols and agreements or simply due to new laws and regulations regarding the restriction in increase of nation-wide carbon footprint. Most notable examples of such protocols and regulations are the “Kyoto Protocol” under the United Nations Framework Convention on Climate Change and the “Cap and Trade” policy by the Environmental Protection Agency in the United States. Furthermore, with advancement of science and breakthrough of promising new technologies this transition to green energy sources is becoming increasingly achievable.

Catalytic conversion of biomass to biofuels or for the production of hydrogen has gained a remarkable attention in the past decade and enhancement of catalysts used for these processes have thus been widely studied. In particular, formic acid, containing 4.4 wt% hydrogen, is a by-product of many chemical processes and is thus a promising hydrogen storage source. As an example, formic acid is produced alongside levulunic acid in an intermediate step for the conversion of cellulose to gamma-Valerolactone (GVL), a green biofuel, represented in Figure 1. Formic acid, through decomposition, is able to serve as a source of hydrogen for the reduction
of levulanic acid to gamma-Valerolactone, thus making the last step without the need of an external source of energy.

The literature suggests that although the decomposition of formic acid for the production of hydrogen has been studied, there is still space for improvement for optimization of this catalytic process to maximize hydrogen yield. Several homogeneous and mono-metallic heterogeneous catalysts such as ruthenium and palladium have shown to be promising in terms of catalytic activity. Although bimetallic catalysts have been studied intensively for hydrogen production, the use of such heterogeneous catalysts for decomposition of formic acid has not been reported in the literature. Such catalysts offer great promise due to their tunable properties by adjusting their composition and morhostructure. Due to its moderate catalytic activity and structural stability, ruthenium is frequently used in bimetallic catalyst systems. For example, Ru$_x$Sn$_y$/C has been used for the reduction of levulinic acid to GVL and has proven to be more active than Ru/C, suggesting the superior catalytic activity of the Ru-Sn alloy for formic acid decarboxylation.

**Figure 1: Schematic representation of an integrated process for the conversion of cellulose to GVL using formic acid as hydrogen source**
In this study the use of ruthenium-based bimetallic catalysts for the decomposition of formic acid via the decarboxylation pathway to produce hydrogen and carbon monoxide is examined.

1.2 Objective and Hypothesis

The objective of this project is to synthesize and identify a highly active ruthenium alloy bimetallic catalyst for the decomposition of formic acid in moderate temperatures (i.e. 150 – 180 °C). It is hypothesized that promotion of ruthenium with alkali and alkaline earth metals would positively impact the catalytic activity and structural stability.

1.3 Scope of Project

Several bimetallic ruthenium alloy catalysts are synthesized in this project and their catalytic activity for the decomposition of formic acid are determined under various reaction conditions. Furthermore, a number of catalysts will be characterized by X-ray diffraction and the most promising catalyst will undergo kinetic studies. The effect of presence of sulfuric acid is also examined. This mineral acid is present alongside formic acid and levulinic acid in the final step of the conversion of cellulose to gamma-valerolactone. The separation of sulfuric acid from formic acid, however, will not be discussed.
Chapter 2
Literature Review

2 Literature Review

2.1 Natural Sources of Formic Acid

Natural sources of formic acid include ant venom and vegetation emissions of hydrocarbons that are photo-oxidized to organic acids. [1][2]

2.2 Commercial Production and Synthesis of Formic Acid

Due to the many applications of formic acid, most notably hydrogen storage in liquid phase, commercial production of this simple carboxylic acid has faced substantial increase in the past decades. These commercial methods of production include:

- Reaction of formates with strong mineral acids
  - This is the first method of commercial production of formic acid. Sodium formate (or calcium formate) reacts with sulfuric acid or nitric acid (strong mineral acids) to produce formic acid. However, the high cost of reactant formates degrades the feasibility of this method. [3]

- Hydrolysis of methyl formate [3]
  - This is a two-step process of production of formic acid. In the first step, methyl formate is formed by methanol carbonylation with CO as shown in $R.1$.

$$ CH_3OH + CO \rightarrow HCH_3CO_2 $$

$R.1$

- The second step consists of production of formic acid and methanol with hydrolyzing methyl formate as stated in $R.2$. 


\[ HCH_2CO_2 + H_2O \rightarrow HCOOH + CH_3OH \quad R.2 \]

- Hydrolysis of formamide [4]
  - The first step is the production of methyl formate as shown in \textit{R.1}. The following step is the ammonylation of methyl formate to produce formamide, which is then hydrolyzed by sulfuric acid to produce formic acid and ammonium sulfate, as shown in \textit{R.3}.

\[ HCONH_2 + \frac{1}{2}H_2SO_4 + H_2O \rightarrow HCOOH + \frac{1}{2}(NH_4)_2SO_4 \quad R.3 \]

- By-product of oxidation of hydrocarbons to acetic acid
  - This catalytic process involves a hydrocarbon such as butane or naphtha, in liquid phase, and a metal catalyst such as cobalt or manganese.
  - Oxidation of butane with manganese yields more formic acid than with cobalt catalyst, as the yields from the reactions with the two catalysts are reversed with respect to the primary product, acetic acid. [3][5]

- Catalytic hydrogenation of \( CO_2 \)
  - Carbon dioxide could be used as the raw material of synthesis of formic acid, as well as the solvent for the reaction in supercritical state. [6][7]
  - Several catalysts, such as ruthenium, rhodium, palladium and titanium have been studied in the selective hydrogenation of \( CO_2 \) to formic acid in different solvents. Furthermore, these studies have triggered the development of production of other oxygenates using homogenous catalysts. [6][8]
• Catalytic conversion of bio-based carbohydrates to formic acid using molecular oxygen
  o Another interesting approach to the production of formic acid is the conversion of biomass to formic acid using molecular oxygen as the oxidant. In this process, as presented by Wolfel and Taccardi [9], carbohydrates produced from the photosynthesis of plants are oxidized to formic acid and carbon dioxide. The carbon dioxide produced as the by-product of formic acid could thus be used up by the plant for further photosynthesis.
  o Furthermore, conversion of biomass to formic acid has been also studied with hydrogen peroxide as the oxidant in presence of alkali, which resulted in a 75% yield in moderate temperatures. [10]

• By-product of conversion of glucose to Levulinic Acid
  o Formic acid could be synthesized as a by-product in the conversion of cellulose to Y-Valerolactone (GVL), a green bio-based chemical. In this process, C6-sugars, along with water and mineral acids (sulfuric or hydrochloric, 0.1-1.25 M) react to form levulinic acid, formic acid, and the mineral acid used as reactant. [11] Separation techniques such as liquid-liquid extraction are then carried out to extract the mineral acid out of the organic levulinic acid. The greatest portion of the formic acid is taken out with the aqueous extract. However, traces of formic acid remain within the raffinate with the organic phase levulinic acid, which would later act as a poison in the hydrogenation of levulinic acid to GVL. Furthermore, the bimetallic catalysts for decomposition of formic acid are not advantageous in the presence of sulfuric acid. Thus, the formic acid should be separated from the aqueous phase and decomposed to better act as the hydrogen donor in the reduction of LA to GVL.
Another approach with respect to the use of formic acid as the hydrogen donor in this process is the direct synthesis of GVL from C6-sugers without the isolation of the intermediate levulinic acid. Heers et al. [12] have reported that the use of an acid catalyst along with a hydrogenation catalyst, with the formic acid as the hydrogen donor is required throughout this process. Examples of the catalysts used to date for this process are Ru/C for hydrogenation and trifluoroacetic acid (TFA) as the acid catalyst along with formic acid as the hydrogen donor. Other examples of this approach are limited in number especially with the use of homogeneous catalysts.

2.3 Applications of Formic Acid

Due to the physical properties of formic acid, it is considered a safe source of hydrogen. It is liquid at room temperature and is thus an easy-to-handle storage material. [13] As hydrogen is considered one of the important rising energy vectors for its applications in the fuel cell industry, formic acid is also attracting attention by possessing hydrogen. Furthermore, without being initially decomposed to produce hydrogen to be used in proton exchange membrane (PEM) fuel cells, formic acid has also been directly used in another type of fuel cell. Direct Formic Acid Fuel Cells (DFAFC) has been recently studied in more depth and proven to be a promising substitute to small portable fuel cell applications. [14] Formic acid is also used in leather and textile industries for tanning and dyeing and also it is also consumed in silages. In 1998, as reported by BASF, 35% of the manufactured formic acid was used in silages, while 25% was used in textiles and leather industry, and the other 40% was divided in pharmaceuticals, crop-protection agents, latex and rubber auxiliaries and miscellaneous uses. [15]
2.4 Decomposition of Formic Acid

Formic acid, containing 4.4 wt% hydrogen, needs to be decomposed to convert to molecular hydrogen as a by-product.[16] Formic acid decomposes by two different pathways: decarboxylation shown by $\text{R.4}$ or decarbonylation shown by $\text{R.5}$. The former, also called dehydrogenation, produces hydrogen and carbon dioxide, while the latter, also called dehydration, produces carbon monoxide and water. [17][18][19]

$$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \quad \text{R.4}$$

$$\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O} \quad \text{R.5}$$

Both reactions are exergonic reaction with $\Delta G$ of -48.4 kJ mol$^{-1}$ and -28.5 kJ mol$^{-1}$ for $\text{R.4}$ and $\text{R.5}$ respectively. [17]

Formic acid decomposition has been recently studied experimentally and theoretically in detail. The aqueous phase experiments indicate the primary decomposition pathway is decarboxylation due to greater CO$_2$ yield compared to CO. On the other hand, the dehydration decomposition pathway is more favourable than decarboxylation in the gas phase experiments. [20] The reason for this could be explained by the higher activation energy required for the decarboxylation reaction in the absence of water. [21][22] Water reduces the activation barrier and acts as a homogeneous catalyst in decomposition of formic acid. [20]

2.5 Catalyst Design

Production of hydrogen through formic acid decarboxylation is a catalytic process. Furthermore, the decarbonylation pathway, producing CO, is to be minimized in the decomposition of formic acid, due to the poisonous activity of CO in some fuel cells. This section mentions and discusses several different homogenous and heterogeneous catalysts previously used and studied for the
aforementioned process with a brief introduction to the scientific background of heterogeneous catalysts.

2.5.1 Homogeneous Catalysis

The use of homogeneous catalysts for hydrogen production via decomposition of formic acid is less developed than the heterogeneous catalysts approach. [13][23] Coffey, in 1967, showed the use of several soluble metal complexes containing ruthenium, platinum and iridium phosphine complexes, of which the iridium phosphine complexes were reported to be the most active. [24] Rhodium and iridium iodocarbonyl compounds, along with hydrochloric acid were tested in moderate temperatures with a reported turnover frequency (TOF) of 4.4 h⁻¹. [25] More recently, Loges et al. reported higher volumes of hydrogen produced in the presence of tertiary amine ligands, such as N,N-dimethylhexylamine and N,N-dimethylaminoethanol. [26][27]

Fellay et al. reported the use of hydrophilic ruthenium-based catalysts prepared from meta-trisulfonated triphenylphosphine (TPPTS) and [Ru(H₂O₂)₆]²⁺ or RuCl₃. In their continuous system, they found an increasing rate of formic acid decomposition with increasing temperature with a maximum conversion of 95% at a temperature range of 70 °C to 120 °C. Furthermore, their ruthenium-based catalyst was stated to be highly stable as it maintained its activity for a year in solution. [28]

2.5.2 Heterogeneous Catalysis

Since 1912, heterogeneous catalysts have been used and studied for the decomposition of formic acid, with Sabatier being the first to have reported such use. [29] Heterogeneous catalysts generally consist of three components; active catalytic phase, promoter, and support.
The active catalytic phase could be a metal (Pt, Pd, Ru, Ni), a metal oxide (CuO), or a metal sulfide (MoS\(_2\)) that is dispersed in the pores of the support. The active site of a catalyst is thus a collection of atoms responsible for directly catalyzing a chemical reaction. Of the three types of active catalytic phases, metals are used for catalyzing hydrogenation; steam reforming, hydrocarbon reforming, dehydrogenation, Fischer-Tropsch, and oxidation reactions. Most commonly used metals for these reactions are iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, iridium, platinum, and gold. [30][31]

Promoters are added in order to increase the activity (chemical promoters) and/or to enhance the stability (textual promoters) of the catalyst. Example of promoters include metal oxides such as Al\(_2\)O\(_3\), SiO\(_2\), MgO and alkali or alkaline earth metals or metal oxides such as cesium, barium, tin, calcium, sodium, or K\(_2\)O and PbO. Metal promoters are added as dissolved metal salts either singly or in multiples. The order of addition of promoters for multi-promoted catalysts is of importance and could result in different catalytic activity. [30] This matter is discussed in detail in Section 3.1 – Catalyst Design.

The support or the carrier of a heterogeneous catalyst is a stable, high surface area metal oxide or activated carbon. It provides potential sites for the active metal within its pores. Furthermore, the support is primarily responsible for the stability of the catalyst. Carriers or supports have large surface areas of 1.5 to 1500 m\(^2\)/g and pore diameters of 0.4 to 2000 nm. Activated carbon (BET area of 500–1500 m\(^2\)/g), zeolites (BET area of 500-1000 m\(^2\)/g), silica gels (BET area of 200–6000 m\(^2\)/g), activated clays (BET area of 150 – 225 m\(^2\)/g), activated Al\(_2\)O\(_3\) (BET area of 100 – 300 m\(^2\)/g) and Celite 296 (BET area of 4.2 m\(^2\)/g) are the common supports in the order of decreasing surface area. Titania and MgO are some examples of less common commercially used carriers. [30]
2.5.3 Heterogeneous Catalysts Used for Decarboxylation of Formic Acid

Recent studies on decomposition of formic acid by the means of heterogeneous catalysis have been carried out to promote the decarboxylation pathway for optimum hydrogen production. Yi et al. recently reported the effectiveness of atomically dispersed gold on ceria (Au/CeO$_2$) catalyst for the gas phase conversion of formic acid. The catalytic performance and selectivity of this catalyst was reported to be very high at a wide range of temperatures. Carbon dioxide and hydrogen began to form at temperatures as low as 75° C and 50° C respectively. Using their system for gas phase formic acid (3.3 mol% in pure He) decarboxylation, 100% conversion was achieved at the temperature of 175° C. Thus, the rate, reported as the turnover frequency (TOF), is of use when other catalysts are to be compared with this Au/CeO$_2$ for activity. The reported TOF was 0.63 s$^{-1}$ at 130 °C. Furthermore, the addition of 3% water to the stream of 3.3 mol% formic acid/helium had no effect on the conversion of formic acid and the hydrogen selectivity. [32]

In another recent study, Gan et al. have reported the structural stability advantages of their synthesized heterogeneous catalyst, prepared by ruthenium(II) dimer [RuCl$_2$(mTPPTS)$_2$]$_2$ with phosphine-modified MCM-41 mesoporous silica. Four unique catalysts, with different ruthenium loadings on silica were tested. Solution of 10 M formic acid/sodium formate with a ratio of 9:1 was subjected to decomposition at varying reaction conditions. 95% conversion was achieved at 90° C with a TOF of 480 h$^{-1}$. [33]

O’Neil et al. conducted a kinetic study on the decarboxylation of formic acid over carbon-supported palladium catalysts. In this study, carried out in Dr. Dumesic’s laboratory at the University of Wisconsin, Pd/C catalyst exhibits a TOF of 0.075 s$^{-1}$ for the decomposition of 2 M formic acid at 150 °C. The selectivity towards the decarboxylation pathway was reported to be
97%, which suggests that Pd/C is a promising catalyst for the production of hydrogen from formic acid. Moreover, no cocking was observed at the surface of Pd/C catalysts since no methane was produced during the reaction, resulting in a high catalyst stability. [19]

Deng et al. reported the effective use of three synthesized ruthenium based bimetallic catalysts for the decomposition of formic acid and also for the hydrogenation of levulinic acid in the presence of the products from formic acid decarboxylation. \((\text{CH}_2)_3\text{NH}_2\text{-RuCl}_2/\text{SiO}_2, (\text{CH}_2)_3\text{PPh}_2\text{-RuCl}_2/\text{SiO}_2\) and \((\text{CH}_2)_3\text{SH-Cl}_2/\text{SiO}_2\) exhibited TOFs of 1428 h\(^{-1}\), 7357 h\(^{-1}\) and 3295 h\(^{-1}\) respectively. The initial formic acid concentration was 4 M in a solution with sodium formate, at 120 °C carried out for 1 hour. [34]

### 2.6 Conclusion

Ruthenium has shown to be a promising catalyst for the decomposition of formic acid in both homogeneous and heterogeneous approaches. However, there is lack of research conducted on the use of bimetallic catalysts for this process. In principle, bimetallic catalysts can be designed to be more structurally stable than mono-metallic catalysts. Thus, the principal motivation of this study is the development of bimetallic ruthenium catalysts for hydrogen production from formic acid with superior activity and structural stability.
3 Experimental

Experimental methodology and procedures are explained in detail in this section along with the apparatus and the equipment used for formic acid decomposition and product analysis.

3.1 Catalyst Preparation

Several metal promoted ruthenium catalyst were examined and analyzed for formic acid decomposition. Carbon-supported-metal-promoted ruthenium catalysts were prepared by wet impregnation method (see Section 3.1.1 – Wet Impregnation Method). More specifically, cesium-promoted ruthenium over carbon, tin-promoted ruthenium/carbon and barium-promoted ruthenium/carbon were prepared with impregnation of 5% Ru/C (Sigma Aldrich, Oakville) with CsNO\(_3\) (Sigma Aldrich, Oakville), SnCl\(_2\) \(\cdot\) 2H\(_2\)O (Sigma Aldrich, Oakville), and Ba(NO\(_3\))\(_2\) (Sigma Aldrich, Oakville) respectively. Nitrates were chosen over carbonates for cesium and barium salts due to their lower melting points, and hence lower reduction temperatures. High reduction temperatures are not desirable since ruthenium is suspected to sinter at carbonate decomposition temperatures (around 600 °C). Furthermore, only carbon-supported catalysts were studied, as the support was reported to have no effect on the catalytic activity or stability. [19] Cesium-tin-promoted ruthenium on carbon (Ru/C) catalysts were also prepared using the single-stage wet impregnation method, in an aqueous solution containing nitric acid cesium salt and tin chloride dehydrate.
Several catalysts were prepared with different metal:Ru mole ratios ranging from 1:2 to 1:5. After the addition of 5% Ru/C to metal salt solution, catalysts were dried at 80° C for 12 hours in Cole Parmer, Stable Temp oven and then reduced at 450° C for 2 hours in helium and hydrogen medium to form Cs-Ru/C, Sn-Ru/C, and Cs-Sn-Ru/ (see Section 3.1.2 – Catalyst Reduction).

3.1.1 Wet Impregnation Method

Ruthenium catalysts containing tin, barium and cesium with various metal to ruthenium mole ratios were prepared using the wet impregnation method. The desired amount of metal salt (i.e. tin chloride dihydrate, cesium nitrate and barium nitrate) was dissolved in water and the solution and Ru/C catalyst was added to this solution. The mixture was then stirred before being placed in an oven to dry overnight.

Concentration of metal salt solution was varied depending on the salt molecular mass and based on the desired Ru:metal mole ratio (see Appendices: A1 – Wet Impregnation Method).

3.1.2 Catalyst Reduction

After drying, catalysts were reduced in a custom-made flow-through reactor. This system consisted of a ½ inch Quartz Tube, a Thermo Scientific Thermolyne tubular furnace equipped with Eurotherm 2116 temperature controller, two AALBORG GFM mass flow meters and hydrogen and helium gas cylinders. The catalyst sample was positioned in the middle of the Quartz Tube that was placed inside the tubular furnace such that both ends of the tube stuck out of the furnace. One end of the tube was connected to a combined stream of helium and hydrogen flowing into the tube while the other end was open to the atmosphere. The helium and hydrogen cylinders were both connected to a separate mass flow meter and their mass flow rates were controlled at 30 sccm and 15 sccm, respectively. The inlet stream was let to flow over the catalyst for 15 minutes prior to heating. All catalysts were reduced at 450 °C for 2 hours and then
cooled down with helium passing through for 20 minutes. *Figure 2* is a schematic representation of the setup apparatus.

![Figure 2: Schematic representation of the flow reactor for catalyst reduction](image)

### 3.2 Experimental and Apparatus

Decomposition reactions were all carried out in a batch reactor system. Parr 4766 300ml pressure vessel was used as the reactor. The reactor was equipped with a Parr Type J thermocouple, Span 03-4769-T analog pressure gauge and two valves for argon inlet and sampling. The sampling valve was connected to a CeComp Electronics 0-500 PSIG digital pressure gauge for accurate pressure readings. The system was purged and pressurized to 50 psi with argon prior to the reaction and also stirred using a Corning Stirrer PC-353 and a magnetic stir bar during the reaction. Formic acid, nano-pure water and in some cases sulfuric acid and the catalyst were
loaded into the reactor and were brought to the desired temperature using a temperature controller system. A Powerstat variable autotransformer Type 116B controlled the voltage input for the heating system. This variable autotransformer was connected to a Hanyoung NX4 temperature controller that was attached to the heating tape wrapped around the Parr reactor. The variable autotransformer was set to 70% of its capacity. The heating system had a maximum temperature overshoot of 2 °C. After the reaction, digital pressure gauge connected to the sampling valve was disconnected and gas sample was collected using a gas bag. All the experiments were carried out for 1 hour (except for the rate determining experiments). Thus, the varying parameters of the experiment were the reaction temperature, feed concentration, type of catalyst, catalyst loading, and the presence and amount of sulfuric acid. Figure 3 is a schematic representation of the experimental apparatus.

Figure 3: Schematic Representation of the Experimental Apparatus
3.2.1 Presence of Sulfuric Acid at Various Temperatures

Catalyst-free experiments were carried out in the presence of 0.5 M sulfuric acid in the feed. 5% by weight formic acid in 50 g solution of water and 0.5 M sulfuric acid were subject to batch reaction at five different temperatures ranging from 120 °C to 250 °C. The same experiments were also repeated without the presence of sulfuric acid at the same temperatures.

3.2.2 Effect of Ru$_x$Sn$_y$/C in the Presence and Absence of Sulfuric Acid

Ru$_x$Sn$_y$/C catalysts with different Ru:Sn mole ratios were examined, along with 5% by weight formic acid in 50 g solution of water and 0.5 M sulfuric acid at 180 °C for 1 hour. The catalyst loading for all experiments was 0.1 g. Furthermore, the reactions were repeated with the same catalysts and no sulfuric acid at 120 °C. The experiments at this lower temperatures were carried out to observe the effect of temperature on the final conversion of formic acid after 1 hour.

3.2.3 Effect of Catalyst Loading and Temperature

To determine the effect of the catalyst loading on the final conversion of formic acid, the weight of catalyst was doubled in these experiments. Ru/C and five different Ru$_x$Sn$_y$/C catalysts were used at two different reaction temperatures of 120 °C and 180 °C. These reactions were carried out in the absence of sulfuric acid. The amounts of catalyst were 0.1 g and 0.2 g for 180 °C and 120 °C reactions, respectively. Formic acid concentration was kept constant at 5 wt% in 47.5 g water.

3.2.4 Catalyst Stability

Stability of Ru$_x$Sn/C catalyst in terms of catalytic activity and structure was examined. This bimetallic catalyst was used consecutively under identical reaction conditions for 6 times. The
reaction conditions were 0.1 g catalyst in 50 g of 5 wt% formic acid solution at 180 °C with a reaction time of 1 hour. After each run, the solution was centrifuged with Beckman Coulter Allegra™ 25R Cengtrifuge (5200 rpm for 20 minutes) and the catalyst was separated from the remaining formic acid and water solution prior to use for the subsequent experiment. The separated catalysts were not weighed as some catalyst adhered to the reactor interior surfaces and could not be removed with the solution. The reactants (i.e. water and formic acid) were added to the recovered catalyst in the centrifuge vial and then added to the reactor for the next experiment. For comparison, monometallic Ru/C was also tested for catalyst stability under the same conditions.

3.2.5 Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD)

A fresh sample of Ru/C, a fresh sample of Ru₃Sn/C, a used sample of Ru₃Sn/C (used once for formic acid decomposition and stored in water for 1 month), were characterized using JEOL JSM-6610LV Scanning Electron Microscope. Three different detectors were used for particle size determination and element identification for the samples. Secondary electron imaging (SEI) was used for Ru/C and Ru₃Sn/C particle size determination from analyzing the image. Furthermore, backscatter electron composition (BEC) for imaging along with energy-dispersive X-ray spectrometry (EDS) were used for determination of existence of carbon, ruthenium and tin in the test sample. All the images were analyzed with JEOL Scanning Microscope PC Program.

To analyze the interactions between the metals and observe the effect of the metal particle size, fresh and used samples of Ru/C and four different RuₓSnᵧ/C catalysts were characterized with X-ray diffraction, using a Philips XRD system with PW 1830 HT generator.
3.2.6 Reaction Kinetics

Reaction kinetics studies were carried out over Ru$_3$Sn/C to determine the reaction rate profile, reaction rate constant, activation energy, pre-exponential factor and turnover frequency for the catalyst. For this set of experiments, the catalyst activity in terms of final formic acid conversion was calculated at 180 °C and 150 °C for different reaction durations of 0, 15, 30, 45, 60 and 75 minutes. The reaction medium in all the experiments contained 50 g solution of 5% by weight formic acid in 47.5 ml water and 0.1 g catalyst.

3.2.7 Gas Chromatography

Sample product gas collected after each of the abovementioned reactions were analyzed using Hewlett Packed 5890 Series II Gas Chromatographer represented in Figure 4. The oven, injector and detector of the GC all operated at 140 °C. Argon was used as carrier gas for the GC with an inlet pressure of 28 psi to the 1-2392-U Supleco 15 ft by 1/8 inch metal packed GC column. 0.6 ml of the sample, collected in a gas bag after the reaction, was injected into Injector B of the GC using a 1 ml Agilent Manual Syringe. The retention times of hydrogen, carbon dioxide and carbon monoxide were 2, 4 and 13 minutes respectively. The data from the GC was then interpreted by OriginPro 8 and final conversion calculated with the aid of MS Office Excel.
Figure 4: Schematic representation of the gas chromatography apparatus
Chapter 4
Results and Discussion

4 Results and Discussion

In this section the results for the activity, stability and characterization of monometallic and bimetallic ruthenium catalysts for decomposition of formic acid are represented and discussed. Furthermore, kinetic studies carried out will be presented in detail at the end of this section.

4.1 Promotion of Ruthenium/Carbon

Several samples of carbon-supported ruthenium were first promoted with cesium, tin or barium by the means of wet impregnation method. The metals were added at four different loadings, resulting in different metal to ruthenium mole ratios of 0.17, 0.2, 0.25, 0.33 and 0.5. The reaction conditions for this set of experiments were 0.1 g catalyst, 5 wt% formic acid in a 50 g solution with water at 180 °C for 1 hour. The resulting product gas from each catalytic reaction was analyzed and individual product yields plotted in Figure 5, Figure 6 and Figure 7 for Ru_xCs_y/C, Ru_xBa_y/C and Ru_xSn_y/C respectively.
Figure 5: Product yield for 0.1 g Ru₉Csₜ/C, 5 wt% FA, 50 g solution, 180 °C for 1 hour

Figure 5 confirms that formic acid primarily underwent the decarboxylation pathway with the use of Ru₉Csₜ/C as more hydrogen and carbon dioxide was produced compared to carbon monoxide for the five different Cs:Ru mole ratios. However, there was a small amount of carbon monoxide also produced via decarbonylation and water gas shift reaction which is undesirable for the purpose of hydrogen production.
Figure 6: Product yield for 0.1 g Ru$_x$Ba$_y$/C, 5 wt% FA, 50 g solution, 180 °C for 1 hour

In comparison to Ru$_x$Cs$_y$/C, Ru$_x$Ba$_y$/C was a better catalyst for hydrogen production as evident by the higher hydrogen yield represented in Figure 6. This catalyst caused the formic acid decomposition to mainly undergo the decarboxylation pathway, with formation of small amounts of carbon monoxide via decarbonylation and water gas shift reaction. However, the carbon monoxide yield from Ru$_x$Ba$_y$/C was lower than Ru$_x$Cs$_y$/C for all five different metal:Ru mole ratios.
Figure 7: Product yield for 0.1 g Ru$_x$Sn$_y$/C, 5 wt% FA, 50 g solution, 180 °C for 1 hour

From Figure 7, Ru$_x$Sn$_y$/C had the highest hydrogen and carbon dioxide yields compared to Ru$_x$Cs$_y$/C and Ru$_x$Ba$_y$/C. Not only the tin-promoted ruthenium catalyst exhibited the highest activity for formic acid decomposition via decarboxylation, it also resulted in lower amounts of produced carbon monoxide. A maximum hydrogen yield of 13 mmol/g was resulted at the Sn:Ru mole ratio of 0.33. This value was 6 mmol/g and 7.5 mmol/g higher than the hydrogen yields of Ru$_x$Ba$_y$/C and Ru$_x$Cs$_y$/C, respectively, at similar metal:Ru mole ratios. Interactions between formic acid and active sites on the catalysts are responsible for the peak of hydrogen and carbon dioxide yield. In the decarboxylation process, hydrogen (either the carbolic hydrogen or the hydroxide group hydrogen) is adsorbed on the Ru$_x$Sn$_y$ site. The second bond scission follows and the other hydrogen gets adsorbed on the catalyst site. The distance between the two adsorbed
hydrogen ions is dictated by the RuSn alloys. Thus, the availability of adjacent active sites is varied by Ru:Sn mole ratios and optimized at 3:1.

Figure 8: RuCs, RuSn and RuBa, 0.1 g catalyst, 2.5 g FA, 47.5 g water at 180 °C for 1 hour

As plotted in Figure 8, the overall formic acid conversion was also significantly higher for Ru₈Sn₄/C compared to Ru₈Cs₄/C and Ru₈Ba₄/C catalysts at the same metal:Ru loadings. Among the tested Ru₈Sn₄/C catalysts, the highest conversion, 67.5% at 180 °C with the reaction time of one hour, was achieved with the mole ratio of 3Ru:1Sn. It was thus concluded that out of the three metal promoters, tin was the better choice due to its higher catalytic activity and hydrogen selectivity. Therefore, the activity and stability of Ru₈Sn₄/C catalyst for the decomposition of formic acid was examined in more details and results are presented in the subsequent sections.
4.2 Effect of Reaction Temperature on Ru$_x$Sn$_y$/C

The effect of temperature on the decomposition of formic acid was investigated by repeating the experiments demonstrated in Figure 8 at 120 °C and results were compared to those obtained at 180 °C in Figure 9. Other reaction conditions were kept as 0.1 g catalyst, 5 wt% sulfuric acid in 50 g solution with water at the respective temperatures for 1 hour.

Figure 9: 0.1 g Ru$_x$Sn$_y$/C, 5 wt% FA, 47.5 g water at 180 °C and 120 °C for 1 hour
As suspected, conversion of formic acid is significantly lowered by reduction in reaction temperature. Individual product yields for these sets of experiments were also calculated and plotted in Figure 10 and Figure 11 for 180 °C and 120 °C respectively.

Figure 10: Product yield for 0.1 g RuₓSnᵧ/C, 5 wt% FA, 50 g solution, 180 °C for 1 hour
Figure 11: Product yield for 0.1 g Ru$_x$Sn$_y$/C, 5 wt% FA, 50 g solution, 120 °C for 1 hour

*Figure 10* and *Figure 11* confirm that formic acid primarily underwent the decarboxylation pathway at both reaction temperatures. The optimal Sn:Ru ratio shifted to higher mole ratios (~0.8) at the lower temperature of 120 °C. Moreover, carbon monoxide formation via decarbonylation was also observed at 180 °C. Nevertheless, the amount of CO production was minimal and hardly contributes to the higher overall formic acid conversion at elevated temperatures.

### 4.3 Effect of Catalyst Loading

In the next set of experiments, the amount of catalyst was doubled to 0.2 g in the reactions with the temperature of 120 °C and the resulting formic acid conversions were compared to those from experiments with 0.1 g Ru$_x$Sn$_y$ at 180 °C. The reaction conditions for this set of
experiments were 0.2 g Ru/C and Ru\textsubscript{x}Sn\textsubscript{y}/C, 2.5 g formic acid, 47.5 g water at 120 °C for one hour.

![Graph](image)

**Figure 12: Effect of catalyst loading on total formic acid conversion, 5 wt% FA in water, 50 g solution, 1 hour**

Four heterogeneous catalysts with distinct Sn:Ru molar ratios, ranging from 0 to 2, were examined at 120 °C and 180 °C. As evident from Figure 12, a temperature increase of 60 °C (from 120 °C to 180 °C) has a substantially higher effect on the conversion of formic acid than does doubling the catalyst loading from 0.1 g to 0.2 g. Based on this figure, in all cases, the reaction conducted at the higher temperature resulted in a higher formic acid conversion, although the amount of catalyst used was half of the amount used in the experiments carried out at 120 °C.
Figure 13, along with Figure 7, further confirm that the effect of catalyst loading was minimal compared to reaction temperature. The maximum hydrogen yield was 5.4 mmol/g at 120 °C with 0.2 g of Ru$_3$Sn/C as oppose to 13 mmol/g formic acid (Figure 7) at 180 °C with half the amount of the same catalyst (i.e. 0.1 g of Ru$_3$Sn/C).

4.4 Effect of Sulfuric Acid

Formic acid is an intermediate by-product of levulinic acid in the production of gamma-valerolactone (GVL) from cellulose. In this process, a strong mineral acid; such as sulfuric acid, is added to cellulose to assist its conversion to levulinic acid and thus remain in both the organic and inorganic phases of the intermediate products. Two sets of experiments were carried out to observe the effect of sulfuric acid on the decomposition of formic acid with and without the use of Sn$_x$Ru$_y$/C catalyst.
4.4.1 Effect of Temperature and Presence of Sulfuric Acid, Catalyst Free

Catalyst-free experiments were carried out at five different temperatures ranging from 120 °C to 250 °C with 5 wt% formic acid in 50 g solution with water. These reactions were repeated with the presence of 0.5 M sulfuric acid and the results in terms of formic acid conversions were plotted in Figure 14.

![Figure 14: Formic acid conversion with 0.5 M and without sulfuric acid as a function of temperature. 2.5 wt% FA, 50 g solution with water. No catalyst is added](image)

As observed in Figure 14, the conversion of formic acid is substantially higher when sulfuric acid is present in the solution for the catalyst-free reactions over a wide range of decomposition temperatures from 120 °C to 250 °C. Formic acid reaches full conversion at 220 °C after one hour in a solution with sulfuric acid. However, in the absence of sulfuric acid the conversion
decreased by more than 65% at the same reaction temperature and reaction time. To better examine the role of sulfuric acid, the yields of individual products with and without sulfuric acid were examined and are represented in Figure 15 and Figure 16 respectively.

**Figure 15: Product yield for 5 wt% FA in water, 0.5 M sulfuric acid, 50 g solution for 1 hour**
The high CO yields represented in Figure 15 confirm that formic acid primarily undergoes the decarbonylation pathway in the presence of sulfuric acid when no heterogeneous catalyst is present. Sulfuric acid could thus be thought of acting as a homogeneous catalyst for decarbonylation under these reaction conditions. However, in the experiments with no sulfuric acid in the solution, formic acid primarily underwent the decarboxylation pathway as confirmed by the product distribution seen in Figure 16.

### 4.4.2 Effect of Feed Concentration on Catalyst Free Experiments

Initial formic acid concentration was varied in an aqueous solution containing 0.5 M sulfuric acid without heterogeneous catalyst addition to observe the effect of this mineral acid on the decomposition pathway of formic acid. Table 1 provides the initial composition of various reactants in these experiments.
Formic acid, in the presence of water, undergoes an initial conversion to formate by releasing an H$^+$ due to hydrogen-oxygen bond breakage as follows:

\[
\text{HCOOH} \rightarrow \text{H}^+ + \text{HCOO}^-
\]

Decarboxylation and decarbonylation then follow by the release of a H$^+$ or OH respectively. However, in a solution with sulfuric acid, that is considerably stronger than formic acid, the extent of the initial dissociation of formic acid is substantially decreased as observed by the formate concentrations in the first two experiments. In this case, sulfuric acid is expected to dissociate completely (i.e. no more H$_2$SO$_4$ remains in the solution) to bisulfate and hydrogen ion:

\[
\text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^-
\]
The dissociation constant of bisulfate, is also higher than that of formic acid (0.012 for bisulfate vs 0.00018 for formic acid). Thus, bisulfate is further dissociated according to:

$$\text{HSO}_4^- \rightarrow H^+ + \text{SO}_4^{2-}$$

As a result, the solution becomes rich in hydrogen ion that hinders the formation of formate ions. Please refer to *Appendices: A2 – Formate Concentration Calculation* for a sample calculation of [HCOO$^-$].

By increasing the initial concentration of formic acid, it is expected that the concentration of formate in the solution and hence the % conversion of formic acid to also increase. This is confirmed in *Figure 17* that shows an increase in the formic acid conversions at higher concentration of formic acid in the feed.

![Figure 17: 0.5 M Sulfuric Acid in water, 50 g solution, 180 °C, 60 mins, catalyst free](image-url)
To further investigate the effect of sulfuric acid in decomposition of formic acid, the products distribution is given in Table 2.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Formic Acid wt%</th>
<th>[H₂SO₄] (mmol/g)</th>
<th>H₂ (mmol/g)</th>
<th>CO (mmol/g)</th>
<th>CO₂ (mmol/g)</th>
<th>CO:CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0</td>
<td>1.55</td>
<td>0.4</td>
<td>0.94</td>
<td>0.04</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.5</td>
<td>1.57</td>
<td>2.07</td>
<td>1.32</td>
<td>1.6</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.5</td>
<td>0.92</td>
<td>3.01</td>
<td>0.62</td>
<td>4.9</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.5</td>
<td>0.61</td>
<td>3.66</td>
<td>0.50</td>
<td>7.3</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>0.5</td>
<td>0.48</td>
<td>4.45</td>
<td>0.45</td>
<td>9.7</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>0.5</td>
<td>0.26</td>
<td>7.86</td>
<td>0.19</td>
<td>40.9</td>
</tr>
</tbody>
</table>

Table 2: Hydrogen, carbon monoxide and carbon dioxide yields at different FA concentrations, 180 °C, 60 mins

The higher yields of carbon monoxide in the experiments in which the solution contains 0.5 M sulfuric acid compared to the yields of hydrogen and carbon dioxide suggests that formic acid partly underwent decarbonylation reaction in these experiments. As seen in Table 2, not only the CO yield was higher, but also the difference between the products yields increased with increasing formic acid concentration in the feed. The CO:CO₂ molar ratio increased as more formic acid was initially added to the solution. It is thus concluded that, in the absence of a heterogeneous catalyst, decomposition via decarbonylation was favored over decarboxylation at higher formic acid concentrations. As a result, for the purpose of optimization of hydrogen production in the absence of a catalyst, sulfuric acid must be separated from formic acid prior to decomposition.
4.4.3    Effect of Ru$_x$Sn$_y$ with the Presence of Sulfuric Acid

Conversion of formic acid (5 wt%) in the presence of 0.1 g of Ru$_x$Sn$_y$/C catalysts and 0.5 M sulfuric acid in water (50 g solution) at 180 °C for 1 hour at various Sn:Ru mole ratios is given in Figure 18. For comparison, conversion for experiments in the absence of sulfuric acid was also plotted on the same graph.
Ru$_x$Sn$_y$/C catalyst significantly increases the total conversion of formic acid in the absence of sulfuric acid, as shown in Figure 18. As seen previously in Figure 14, when no heterogeneous catalyst was present, the conversion of 5 wt% formic acid in 50 g solution with water (without sulfuric acid) after one hour at 180 °C was only 4.54%. By the introduction of 0.1 g Ru$_3$Sn/C to 2.5 g of FA and 47.5 g of water, in the absence of sulfuric acid, the % conversion of FA
increased to a maximum of 67.54%. However, the catalyst activity decreased significantly when sulfuric acid was added to the reaction medium. In this case, the maximum conversion of FA was only about 31%. Furthermore, in the presence of 0.5 M sulfuric acid, Ru:Sn ratio had negligible effect on the formic acid conversion, suggesting that the activity of the catalyst was governed by the active sites on the ruthenium rather than tin in this bimetallic heterogeneous catalyst and that the promotion of ruthenium with tin was ineffective. The individual product yields for reactions with 0.1 g Ru$_x$Sn$_y$/C, 5 wt% FA, 0.5 M sulfuric acid in water, 50 g solution at 180 °C for 1 hour were also examined and plotted in Figure 19.

Figure 19: Product yields for reactions with 0.1 g Ru$_x$Sn$_y$/C, 5 wt% FA, 0.5 M sulfuric acid in water, 50 g solution at 180 °C, 1 hour
The presence of Ru$_x$Sn$_y$/C shifted the decomposition of formic acid towards decarboxylation as confirmed by Figure 19. The presence of sulfuric acid, however, resulted in significant amounts of carbon dioxide formation via decarbonylation.

Due to the poisonous nature of CO for fuel cells, and for effective production of hydrogen via decarboxylation of formic acid, the mineral acid (i.e. sulfuric acid) is best to be separated from the organic acid. Gurbuz et al. suggested reactive extraction via esterification by reaction with an alcohol or alkene as a strategy to remove the mineral acid from the organic phases of formic and levulinic acid. [35] Another method for separation of the acids is via extraction of formic acid from formic acid and sulfuric acid solution by the use of propyl guaiacol (PG), followed by extraction of formic acid from the solution containing PG by water.

4.5 Catalyst Stability

4.5.1 Cyclic Experiments for Monitoring Activity Stability

To examine the quality of the prepared bimetallic catalysts, Ru$_3$Sn/C was subject to cyclic tests and the results were compared to the activities of a sample of Ru/C catalyst without Sn promoter.

The reactions temperatures and times were 180 °C and 60 minutes, respectively, while the feed concentration was 5% by weight with 0.1 g of Ru$_3$Sn/C or Ru/C catalyst. Formic acid conversion was plotted against the cycle number of the experiment (i.e. experiment repetition number) in Figure 20 followed by the product yields for Ru$_3$Sn/C and Ru/C for each cycle number in Figure 21 and Figure 22, respectively. It should be noted that after each run, the catalyst was separated from the solution and dried prior to use in the proceeding experiment. Thus, although catalyst deactivation due to re-use in experiments was the major cause for these results, a small fraction
of the decrease in conversions was due to the loss of catalyst during the process of catalyst recovery.

Figure 20: Conversion of formic acid in cyclic experiments. 0.1 g Ru₃Sn/C and 0.1 Ru/C, 180°C, 60 min
Figure 21: Product yield for cyclic experiments with 0.1 g Ru$_3$Sn/C, 5 wt% FA in water, 50 g solution, 180 °C for 1 hour

Figure 22: Product yield for repeated experiments with 0.1 g Ru/C, 5 wt% FA in water, 50 g solution, 180 °C for 1 hour
According to the above figures, the deactivation of both catalysts followed a similar pattern. Catalyst activity decreased rapidly during the first two cycles and remained stable for the subsequent cycles. Ru$_3$Sn/C exhibited a formic acid conversion of 65.3% in the first run that dropped to 52.7% and 48.2% for the second and third cycles, respectively. On the other hand, Ru/C resulted in 19.6% conversion of formic acid when used fresh, and this value dropped to 11.1% and 8.9% for the second and the third repetitions, respectively. Furthermore, Figure 21 and Figure 22 indicate that the deactivation pattern was consistent in all products for both Ru$_3$Sn/C and Ru/C. The higher yields of carbon monoxide resulted from Ru/C, along with H$_2$:CO$_2$ ratios of substantially lower than 1 suggest the effect of the water gas shift reaction on the final products.

Although both catalysts underwent the same deactivation pattern, Ru/C experienced this to a higher degree when re-used compared to Ru$_3$Sn/C. This becomes more evident by examining the percent change in the conversion of formic acid in subsequent cycles as summarized in Table 3.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>% Conversion Change</th>
<th>% Conversion Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>From-To</td>
<td>Ru$_3$Sn/C</td>
<td>Ru/C</td>
</tr>
<tr>
<td>1-2</td>
<td>-19.3</td>
<td>-43.0</td>
</tr>
<tr>
<td>2-3</td>
<td>-8.6</td>
<td>-20.2</td>
</tr>
<tr>
<td>3-4</td>
<td>-2.7</td>
<td>10.7</td>
</tr>
<tr>
<td>4-5</td>
<td>0.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Table 3: Change in formic acid conversion with repetitive catalyst use*
Hence, stability and activity of Ru/C were both enhanced by promotion with Sn and Ru-Sn alloy formation over the tested experiment conditions.

4.5.2 X-Ray Diffraction

Ru/C and several Ru\textsubscript{x}Sn\textsubscript{y}/C catalysts were further characterized by the means of X-ray diffraction for examination of the interactions between the metals and their particle sizes. Both fresh and used samples of the catalysts were characterized for detection of structural changes due to the catalyst exposure to the reaction environment. Figure 23 demonstrates the results for nine different catalysts with various Ru:Sn ratios.

![XRD Plots for several Ru\textsubscript{x}Sn\textsubscript{y}/C fresh and used catalysts](image)

**Figure 23: XRD Plots for several Ru\textsubscript{x}Sn\textsubscript{y}/C fresh and used catalysts**

The nanoparticles of Ru phase are too small to be detected by XRD (less than 4nm) and thus no indication of it is observed in Figure 23. [36] Metal particles are believed to be well dispersed due to lack of diffraction pattern for Ru/C, Ru\textsubscript{5}Sn/C, Ru\textsubscript{3}Sn\textsubscript{1}/C and RuSn/C catalysts. This is an
indication of the absence of any metal clusters. However, RuSn$_{5}$/C, that is rich in tin, represented peaks (at 44° 2θ) that are proof of tin clusters. Having a particle size of 100nm, tin particles were detectable by XRD. For Sn:Ru mole ratios smaller than 1, including Ru/C, generally no significant change was observed between the fresh and the used samples. The peaks at 27° 2θ could not be identified with the reference Ru, Sn, or RuSn XRD patterns. In another attempt to characterize RuSn with XRD, reported by Wettstein et al., no reflection for Ru was identified over a wide range of 13° to 33° 2θ. [37]

4.6 Scanning Electron Microscopy

Fresh and used samples of Ru$_3$Sn/C and a fresh sample of Ru/C were characterized by SEM for particle size determination and element identification by the means of secondary electron imaging (SEI), backscatter electron composition (BEC) and energy-dispersive X-ray spectrometry (EDS).
Figure 24: SEI images of fresh Ru/C at four different magnifications

*Figure 24* represents the SEI images of fresh Ru/C (5 %wt Ru as purchased from Sigma Aldrich, Oakville). As evident from the images, Ru/C particles had irregular geometries and their particle size lies in the range of 1 - 100 µm, with most particles being closer to the lower limit of this range.
BEC imaging allows for distinct element determination. The brightness of different spots on the image indicate the intensity of the reflected beam of electrons. The brighter the spot, the higher the atomic number of the targeted element. Thus, for Ru/C, ruthenium is represented in Figure 25 by the bright spots (atomic number of 44) and carbon by the darker spots (atomic number of 6). Figure 26 is a close-up SEI image and spectrometry graph of the bright spot on Figure 25 marked by “1”.

**Figure 25: BEC image of fresh Ru/C**
Figure 26: ×3000 magnification and energy spectrometry graph of Ru/C. x-axis has the units of keV
It is confirmed by Figure 26 that the bright spot contains both carbon and ruthenium. The very first large peak represents carbon while the peaks around 2.2 to 2.9 keV represents ruthenium. Some oxygen was also detected in this sample, as indicated by the peak at 0.5 keV, which is the evidence for Ru oxidation. Although the SEM operates in high vacuum conditions, some oxidation may take place while handling the sample and positioning it on the microscope stage.
a) \( \times 100 \) magnification, white line = 100 µm

b) \( \times 300 \) magnification, white line = 50 µm

c) \( \times 1000 \) magnification, white line = 10 µm

d) \( \times 10000 \) magnification, white line = 1 µm

Figure 27: SEI images of fresh Ru\(_3\)Sn/C at four different magnifications
SEI images for a fresh sample of synthesized Ru₃Sn/C, represented in Figure 27, suggest that the catalyst particle size was in the 2 – 200 µm. The particle size of this catalyst was slightly larger than Ru/C due to the addition of tin. Similar to Ru/C, these catalyst particles were also irregular in shape.

![Figure 28: BEC image of fresh Ru₃Sn/C](image)

The BEC image of Ru₃Sn/C is given in Figure 28. Since ruthenium and tin have atomic numbers of 44 and 50, it difficult to distinguish between them with the aid of brightness and contrast in the BEC image. However, the darker regions clearly represent carbon atoms (atomic number of 6). Figure 29 represents the electron energy spectrum for the spot marked with “1” on Figure 28.
The peaks in Figure 29 confirm the presence of carbon, ruthenium, tin and oxygen. The oxygen is an indication of Ru-Sn alloy oxides formation due to exposure of catalyst to air during sample loading to SEM. The main constituent of the catalyst was carbon as represented by the large peak at 0.25 keV. Thus, the bright white color observed on “1” from Figure 28 is the evidence for Ru-Sn alloy dispersed on carbon support.

Figure 29: Energy spectrometry of fresh Ru$_3$Sn/C
SEI images from a used sample of Ru$_3$Sn/C in Figure 30 suggest that the shape and the size of the particles did not change by using and storing the catalyst in water. However, the catalytic activity slightly diminishes as discussed in Section 4.5 – Catalyst Stability.
4.7 Kinetic Studies

Reaction kinetics studies were carried out for formic acid decomposition via decarboxylation with Ru$_3$Sn/C at 180° C and 150° C for determination of reaction rate constant, activation energy and the pre-exponential factor. Determining the rate, along with metal dispersion data obtained from literature allowed for turnover frequency calculations.

4.7.1 Order of Reaction and Reaction Rate Constant

The rate law, with respect to consumption of formic acid is expressed as follows:

\[ r = -k[HCOOH]^n \]

where \( k \) represents the reaction rate constant and \( n \) represents the order of the reaction. The expression is then rearranged as follows:

\[ \frac{d[HCOOH]}{dt} = -k[HCOOH]^n \]

\[ \frac{d[HCOOH]}{[HCOOH]^n} = -k \, dt \]

The above expression was integrated with respect to four different reaction order values of zero, one, two and \( n \) and the resulting conversions were plotted with respect to reaction time to determine the order of reaction.

For this set of experiments, 5% by weight formic acid (2.5 g FA in 47.5 g water) was decomposed at 180° C with 0.1 g Ru$_3$Sn/C.

For first order reaction (\( n = 1 \)), the formic acid concentration is expressed as a function of time:
\[ [HCOOH] = [HCOOH]_0 e^{-kt} \]

*Figure 31* shows that the natural logarithm of formic acid concentration is a linear function of reaction time, suggesting that catalytic conversion of formic acid can be represented by a first order reaction kinetics in terms of formic acid concentration.

![Figure 31: First order kinetics at 180 °C, 0.1 g Ru3Sn/C, 5 wt% FA, 50 g solution](image)

The reaction rate constant, \( k \), that is the slope of the linear plot in Figure 31 was then calculated to be:

\[ k = -(slope \ of \ the \ line) = 1.39 \times 10^{-2} \ \text{min}^{-1} \]
\[ k = 2.33 \times 10^{-4} \text{ s}^{-1} \]

4.7.2 Pre-Exponential Factor and Activation Energy

Using the approach discussed in the previous section, rate constant was calculated for the decomposition reaction at 150 °C to allow for the estimation of the activation energy and pre-exponential factor using the Arrhenius equation. As seen in Figure 32, once decomposition of formic acid at 150 °C followed a first order kinetics with a reaction rate constant of:

\[ k = 3.6 \times 10^{-5} \text{ s}^{-1} \]

![Figure 32: First Order Kinetics at 150 °C, 0.1 g Ru3Sn/C, 5 wt% FA, 50 g solution](image)

Accordingly, using the Arrhenius equation, the activation energy, \( E_a \), and the pre-exponential factor, \( A \), for the decomposition of formic acid were determined to be:
\[ k = A e^{-\frac{Ea}{RT}} \]

\[ Ea = 99.95 \frac{kJ}{mol} \]

\[ A = 7.76 \times 10^7 \text{ s}^{-1} \]

4.7.3 Turnover Frequency

Turnover frequency (or TOF) for a heterogeneous catalyst is an expression of reaction rate in terms of turnover of a catalytic site. Boudart defines TOF as the number of revolutions of catalytic cycle per unit time. [37] It is used for the comparison of reported catalytic activity in literature and it is advantageous over reporting the activity as conversion since TOF takes into account the amount of catalyst used and allows for comparison by a single rate value. TOF is calculated by dividing the reaction rate by the catalyst dispersion.

To estimate the TOF, the initial reaction rate constant for the formic acid decomposition at 180 °C was used, while the dispersion was obtained from the literature. The uptake of molecular oxygen as determined by chemisorption analysis is an indicator of total metal sites.[38] Wettstein et al., reported an O$_2$ uptake of 179 µmol/g for tin-promoted Ru/C catalyst with a Ru:Sn molar ratio of 3.6 Using this value, a TOF of 0.68 s$^{-1}$ was obtained for Ru$_3$Sn/C (see Appendices: A3 – Turnover Frequency Calculation for a sample calculation of the initial turnover frequency).[38] It is important to note that TOF decreases as the reaction moves forward as it is a function feed concentration. Figure 33 represents TOF with respect to the remaining formic acid concentration.
Figure 33: TOF profile of Ru$_3$Sn/C for the decomposition of 5 wt% formic acid

For comparison, Pd/C exhibited a TOF of 0.07 s$^{-1}$ at 150 °C for decomposition of 2 M formic acid as reported by O’Neill et al.[19] The initial TOF resulted from Ru$_3$Sn/C was calculated to be 0.1 s$^{-1}$ with respect to the reaction rate constant at 150 °C. This rate is larger than the TOF of Pd/C at nearly half of the initial formic acid concentration (i.e. 1.09 M). Assuming linear relation between TOF and formic acid concentration, the Ru$_3$Sn/C is expected to exhibit a TOF of 0.19 s$^{-1}$ at a formic acid concentration of 2 M which is nearly 3 times better than the reported TOF of Pd/C. Furthermore, formic acid decomposition catalyzed by RuCl$_3$ and mTPPTS was reported to have a TOF of 0.13 s$^{-1}$ for 10 M at a lower temperature 90 °C. This value is again much lower than the TOF of Ru$_3$Sn/C, considering the fact that the formic acid concentration was also significantly higher.
However, dispersed gold particles on ceria (Au/CeO), with a TOF of 0.63 s$^{-1}$ at 3.3 mol% formic acid in helium (gas phase decomposition) at 130 °C, are considered one of the most active catalysts for the decomposition of formic acid. This activity is comparable to the activity of Ru$_3$Sn/C, although the reactions are of two distinct natures (gas phase and liquid phase). Table 4 summarizes the reaction conditions and TOFs for heterogeneous catalytic decomposition of formic acid reported in the literature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial [HCOOH]</th>
<th>Temperature (°C)</th>
<th>Initial TOF (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru$_3$Sn/C</td>
<td>1.09 M</td>
<td>180</td>
<td>0.68</td>
</tr>
<tr>
<td>Ru$_3$Sn/C</td>
<td>1.09 M</td>
<td>150</td>
<td>0.1</td>
</tr>
<tr>
<td>Pd/C</td>
<td>2 M</td>
<td>150</td>
<td>0.07</td>
</tr>
<tr>
<td>Ru/SiO$_2$</td>
<td>10 M</td>
<td>90</td>
<td>0.13</td>
</tr>
<tr>
<td>(CH$_2$)$_3$NH$_2$-RuCl$_2$/SiO$_2$</td>
<td>4 M</td>
<td>120</td>
<td>0.39</td>
</tr>
<tr>
<td>(CH$_2$)$_3$PPh$_2$-RuCl$_2$/SiO$_2$</td>
<td>4M</td>
<td>120</td>
<td>0.9</td>
</tr>
<tr>
<td>(CH$_2$)$_3$SH-RuCl$_2$/SiO$_2$</td>
<td>4M</td>
<td>120</td>
<td>2</td>
</tr>
<tr>
<td>Au/CeO</td>
<td>3.3 mol% FA</td>
<td>130</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Table 4: TOFs of several heterogeneous catalysts for the decomposition of formic acid

It should be noted that 4 M formic acid was in a solution with sodium formate for experiments with (CH$_2$)$_3$ NH$_2$-RuCl$_2$/SiO$_2$, (CH$_2$)$_3$ PPh$_2$-RuCl$_2$/SiO$_2$ and (CH$_2$)$_3$ SH-RuCl$_2$/SiO$_2$. Therefore,
the dissociation of HCOONa into formate would contribute to a higher amount of formate available for decomposition to H₂ and CO₂, resulting in relatively higher TOFs.
Chapter 5
Conclusion

5 Conclusion
5.1.1 Concluding Remarks

Throughout the reported literature since decades ago, ruthenium catalyst has proven to be a promising catalyst for hydrogen production from conversion of biomass. More recently ruthenium and palladium have been studied and experimented with for the decomposition of formic acid in the field of heterogeneous catalysis. The effect of promoting the ruthenium over carbon catalyst with an alkali metal, an alkaline earth metal and a main group metal for the production of hydrogen via formic acid decarboxylation was examined in this project. The alloy formed by the addition of tin to ruthenium in different ratios substantially increased the catalytic activity and structural stability. Cesium and barium also had positive effects on ruthenium in terms of activity and stability for the aforementioned process. However, tin proved to be the most effective promotion of the three metals.

The synthesized Sn,Ru, catalysts were also experimented with feed mixture of formic acid and sulfuric acid, due to the presence of sulfuric acid alongside formic acid in the conversion of cellulose to levulinic acid. It is concluded that the mono-metallic ruthenium is almost identical to the bimetallic ruthenium-tin catalysts synthesized for this decomposition process in terms of catalytic activity. Furthermore, the conversion of formic acid was higher when no catalyst was present in the feed. This higher conversion, however, is a result of the decarboxylation decomposition pathway taken by formic acid, which produces carbon monoxide and water. Thus, there are two reasons that make the separation of formic acid from sulfuric acid prior to
decomposition reaction beneficial. First is the lower hydrogen yield achieved due to the decarbonylation pathway primarily taken in the presence of sulfuric acid. The second reason is the production of carbon monoxide, which is a poison for many fuel cells.

The Ru$_x$Sn$_y$/C bimetallic catalyst also proved to be more enhanced than Ru/C in terms of structural stability. This conclusion was reached upon by the re-use of the same catalyst throughout consecutive experiments with the same conditions.

5.1.2 Recommended Future Work

This project has the potential to continue with new catalysts. Palladium is also reported to be highly active for the decomposition of formic acid and could thus be promoted with different metals for performance enhancement. More specifically, due to its promising results from this project, it is recommended for the future research to start from promotion of palladium with tin.

Furthermore, multi-promotion of ruthenium and palladium were not considered in this project and thus design of experiments with these catalysts is recommended once the most active promoters are identified.

One of the applications of decomposition of formic acid via decarboxylation is in the conversion of cellulose to gamma-Valerolactone, a green biofuel. However, as mentioned before, the biggest challenge is to work with sulfuric acid, as it is present alongside the organic acid within this conversion process. It is thus recommended that the future work on this project to study the separation of formic acid from sulfuric acid.
References


[29] Sabatier P., Mailhe A. Compt Red 152 (1912) 1212


[34] Deng, Li, Yan Zhao, Jiang Li, Yao Fu, Bing Liao, and Qing-Xiang Guo. "Conversion of Levulinic Acid and Formic Acid into γ-Valerolactone over Heterogeneous Catalysts." *ChemSusChem* 3.10 (2010): 1172-175.


Appendices

A1 – Wet Impregnation Method

The concentration of the salt solution added to 0.3 g Ru/C used for the preparation of Ru₃Sn/C was calculated:

\[ 0.3 \text{ g } Ru/C \to 0.05 \times 0.3 \text{ g } = 0.015 \text{ g Ru} \]

\[ 0.015 \text{ g Ru} \div 101.07 \frac{g}{mol} = 1.48 \times 10^{-4} \text{ mol Ru} \]

\[ 3Ru: 1Sn \to 1.48 \times 10^{-4} \div 3 = 4.95 \times 10^{-5} \text{ mol Sn} \]

\[ 4.95 \times 10^{-5} \text{ mol Sn} \times 225.65 \frac{g}{mol} = 0.0112 \text{ g SnCl}_2 \cdot 2H_2O \]

Thus, 0.0112 g of tin salt was added to 0.3 g of Ru/C for Ru₃Sn/C preparation. The salt was dissolved in 0.285 g of water and added to Ru/C and stirred for one minute. The weight of water that the salt was dissolved in was identical to weight of the support of the catalyst (i.e. 95\% of 0.3 g Ru/C is 0.285 g carbon).

A2 – Formate Concentration Calculation

Formate concentration for the experiment with 50 g solution consisting of 2.5 g formic acid and 0.5 M sulfuric acid and the balance water was calculated using the equilibrium constants of bisulfate and formic acid:

\[ 0.5 \text{ M } H_2SO_4 \to 0.5 \text{ M } H^+ \text{ and } 0.5 \text{ M } HSO_4^- \]

\[ HSO_4^- \to H^+ + SO_4^{2-} \]
Formic acid, with the initial concentration of 0.00112, is then dissociated with 0.512 M $H^+$ already in the solution:

\[
\text{HCOOH} \rightarrow H^+ + \text{HCOO}^-
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.5 M</th>
<th>0.5 M</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>-x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.5 - x</td>
<td>0.5 + x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_{a,bisulfate} = 0.012 = \frac{[SO_4^{2-}][H^+]}{[HSO_4^-]} = \frac{(x)(0.5 + x)}{0.5 - x}
\]

\[
x = 1.15 \times 10^{-2} \text{ M}
\]

\[
[H^+] = 0.5 + x = 0.512 \text{ M}
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.00112 M</th>
<th>0.512 M</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>-x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.00112 - x</td>
<td>0.512 + x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_{a,formic acid} = 0.00018 = \frac{[\text{HCOO}^-][H^+]}{[\text{HCOOH}]} = \frac{(x)(0.512 + x)}{0.00112 - x}
\]

\[
x = 2.57 \times 10^{-7} \text{ M}
\]

\[
[\text{HCOO}^-] = 3.92 \times 10^{-7} \text{ M}
\]
A3 – Turnover Frequency Calculation

The initial formic acid decomposition rate at 180° C was calculated:

\[ r = k[HCOOH]^1 \]

\[ r = 2.3 \times 10^{-4} \text{s}^{-1} \times 1.096 \frac{mol}{L} = 2.52 \times 10^{-4} \frac{mol}{L \cdot s} \]

S is defined as the number of surface sites. TOF is then calculated:

\[ \text{Initial Volume of Solution} = 0.0475 \text{ L water} + \frac{2.5 \text{ g FA}}{1220 \text{ g/L}} = 0.0495 \text{ L} \]

\[ S = 179 \frac{\mu\text{mol}}{g} \times 10^{-6} \frac{mol}{\mu\text{mol}} \times \frac{1}{0.0495 \text{ L solution}} = 3.6 \times 10^{-3} \frac{mol}{L \cdot g} \]

\[ \text{TOF}_{\text{initial}} = \frac{\text{rate}}{\text{number of surface sites}} = \frac{2.52 \times 10^{-5} \frac{mol}{L \cdot s}}{(3.6 \times 10^{-3}) \frac{mol}{L \cdot g} \times 0.1 g} = 0.68 \text{ s}^{-1} \]