TOWARDS HYDROGEN STORING SYSTEMS FOR VEHICULAR APPLICATIONS

by

Vanessa Renee Little

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Abstract

The rising environmental and financial consequences of using fossil fuels as an energy source and energy carrier are a global concern. Described herein are two hydrogen-storing technologies, each of which was envisioned as a potential solution to said consequences: hydrogen-storing polymethylpyridylsiloxanes for use as an alternative energy carrier to fossil fuels; and thermally regenerative fuel cell systems to supplement or supplant vehicular alternators.

A thermally regenerative fuel cell (TRFC) system is being developed to convert waste heat from an internal combustion engine (ICE) system into electricity that can be used to power auxiliary vehicular components. The TRFC system will comprise a dehydrogenation reactor and a fuel cell positioned relative to the ICE system such that the two components are held at 200 °C and 100 °C, respectively. 1-Phenyl-1-propanol has been identified as an optimal hydrogen storing liquid (XH₂) that will selectively dehydrogenate over a heterogeneous catalyst to give a dehydrogenated liquid (propiophenone, X) and H₂. The heterogeneous catalyst that currently provides the best selectivity (99.65%) for X at 200 °C is Pd/SiO₂. A selectivity of ≥ 99.9% was desired to obtain the longest possible operational lifetime for the working fluids XH₂/X. To increase the selectivity for X from 99.65% to ≥ 99.9%, size and shape specific Pd nanoparticles were synthesized. Pd nanocubes (20 nm) provided the best selectivity for X at 99.26%. It was concluded that a reproducible selectivity for X of ≥ 99.9% was not currently obtainable, and that a selectivity for X no greater than 99% should be assumed when calculating the working fluids’ operational lifetime.

Hydrogen-storing polymethylpyridylsiloxanes were proposed as energy carrier
alternatives to fossil fuels. Polymethylpyridylsiloxanes were considered, in part, due to the expansive liquid ranges of siloxane polymers [-40 °C to 250 °C]; this would allow the polymethylpyridylsiloxanes to be stored and pumped into vehicles using existing refueling infrastructure. Polymethylpyridylsiloxanes, and analogs thereof, however, were not successfully synthesized and reversibly hydrogenated: either the desired product(s) could not be synthesized, isolated, and/or purified; or, hydrogenation resulted in product decomposition. It was concluded, therefore, that implementing polymethylpyridylsiloxanes as hydrogen-storing liquids is not viable.
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Statement of Originality

I hereby certify that all of the work described within this thesis is the original work of the author. A version of Chapter 2 and Chapter 4, in part, has been described in Carrier, A.; Dean, D.; Little, V. R.; Vandersleen, J.; Davis, B.; Jessop, P. G. Energy Environ. Sci. 2012, 5, 7111–7123. A version of Chapter 3, in part, has been described in Little, V. Heterocyclic Functionalized Siloxane Polymers as Hydrogen-Storing Liquids. PhD Candidacy Examination, Chemistry, Queen’s University: Kingston, Ontario, 2009. Any published (or unpublished) ideas and/or techniques from the work of other researchers and collaborators are fully acknowledged in text and/or accordance with the standard referencing practices. In particular, Section 3.6.5 of Chapter 3 was done in collaboration with Dominique Vanier, BSc, as previously described in Vanier, D. Functionalized Polysiloxanes as Hydrogen-Storing Liquids. Chemistry Honours, 2009 and Little, V. Heterocyclic Functionalized Siloxane Polymers as Hydrogen-Storing Liquids. PhD Candidacy Examination, Chemistry, Queen’s University: Kingston, Ontario, 2009.

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List of Symbols and Abbreviations

aka also known as
Ar argon\(_{(g)}\)
°C degrees Celsius
\(^{13}\)C carbon isotope, mass: 13 amu
COSY homonuclear correlation spectroscopy
2-D two-dimensional
d doublet
dd doublet of doublets
dt doublet of triplets
EI-MS electron impact mass spectrometry
ESI-MS electrospray ionization mass spectrometry
Et ethyl
\(^{1}\)H proton
HMBC heteronuclear multiple bond correlation
HPLC high performance liquid chromatography
HR high resolution
Hz hertz
HSQC heteronuclear Single Quantum Correlation
ICE internal combustion engine
ICP-MS inductively coupled plasma mass spectroscopy
ICP-OES inductively coupled plasma optical emission spectrometry
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>IUPAC</td>
<td>international union of pure and applied chemistry</td>
</tr>
<tr>
<td>J</td>
<td>coupling constant</td>
</tr>
<tr>
<td>kg</td>
<td>kilogram</td>
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<td>M</td>
<td>moles per liter</td>
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<td>MALDI</td>
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</tr>
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<td>Py</td>
<td>pyridine</td>
</tr>
</tbody>
</table>
q   quartet
qt  quartet of triplets
RB  round bottom
RT  room temperature
s   singlet
SBA-15  Santa Barbara amorphous mesoporous silica type 15
SEM  scanning electron microscope
29Si  silicon isotope, mass: 29 amu
SPS  solvent purification system
t   triplet
TCL  thin layer chromatography
TEM  transmission electron microscope
TMS  tetramethyldisilane
TRFC  thermally regenerative fuel cell
tt  triplet of triplets
Δ   heat
ΔX  change in X (e.g. X = H, G, S, etc)
µL  microliters
Chapter 1

Introduction

1.1 The Premise

Human beings are the only species on Earth with the ability to affect very real change on the planet. We have developed the ability to accrue our planet’s resources and shape those resources into the necessities and commodities of life: shelter, transportation, medicine, food, etc. This acquisition and manipulation of resources, however, has not occurred without consequence: the world is being depleted of resources and its climate is changing. In an attempt to develop a more sustainable way of life for mankind, while maintaining and/or improving upon our standard of living, scientists and engineers have focused on developing technologies that will slow or prevent resource depletion and anthropogenic contributors to climate change.

This thesis will focus on the investigation and/or development of two such technologies: a hydrogen-storing siloxane polymer to supplant fossil fuels as an energy carrier, and a thermally regenerative fuel cell system to supplant (or supplement) vehicular alternators to improve fuel efficiency. Either of these technologies, once optimized and implemented, could slow down the depletion of resources (e.g. fossil fuels), and reduce anthropogenic carbon dioxide (CO$_2$) emissions, a greenhouse gas connected to climate change.
1.2 Fossil Fuel Consumption and Carbon Dioxide Emissions

As of 2009, there were over 20 million vehicles on the roads in Canada: 19.8 million were vehicles $\leq 4.5$ tonnes in weight, with the remaining vehicles being $\geq 4.5$ tonnes. Those 20 million vehicles travelled over 333 billion kilometers, and consumed 31.5 billion liters of gasoline and 9.9 billion liters of diesel in total.\(^1\) These are staggering numbers for a country with a population of only 35 million,\(^2\) and it is expected that our fossil fuel demand will only increase. According to the US Energy Information Administration, the global demand for petroleum and other liquids in 2010 was over 80 million barrels per day; by 2035 it is expected for that demand to reach nearly 120 million barrels a day (Figure 1).\(^3\) While it is expected that global demand for fossil fuels will not exceed global production from OPEC and Non-OPEC sources as of 2035,\(^3\) the fossil fuel supply, being a non-renewable resource, will eventually diminish. As such, it is important for society to start shifting its dependence on fossil fuels to other energy sources (resources that provide useful energy, such as human, animal, wind, water, and nuclear power\(^4\)) and/or energy carriers (substances with which energy is transported for on-site use) so that it may continue to meet its energy demands while slowing or preventing the depletion of fossil fuels as a resource.
Figure 1 Global supply and demand for petroleum and other liquids as of 2010 with projections for 2035 (Reproduced with permission from the US EIA Annual Energy Outlook Report, 2012).  

The 333 billion kilometers driven by Canadians in 2009 translated into 73.2 billion kg of CO$_2$ from gasoline and 26.3 billion kg of CO$_2$ from diesel being released into the atmosphere. This is detrimental; CO$_2$ is a greenhouse gas, and its increasing concentration in the Earth’s atmosphere is considered one contributing factor to climate change (a.k.a. the greenhouse effect). An abundance of greenhouse gases in the atmosphere (e.g. carbon dioxide, methane, etc.) can increase the surface temperature of the Earth through positive radiative forcing. When Earth absorbs electromagnetic radiation from the Sun, some of that energy is re-radiated outward as infrared radiation; greenhouse gases in the atmosphere cause that outgoing energy to be reabsorbed and re-radiated back to Earth’s surface, thus warming it. The global average surface temperature has in fact increased by 0.6 ± 0.2 °C since the 19th century. This temperature increase
correlates to an increase in atmospheric concentrations of CO$_2$: during the pre-industrial age, atmospheric CO$_2$ concentrations were essentially constant at 280 ppm; over the span of the 20$^{th}$ century, however, that concentration increased from 280 ppm to 365 ppm. The atmospheric concentration of other greenhouse gases, such as methane and nitrous oxide, has also increased, and thus could also be a contributing factor to the increase in atmospheric temperature (Figure 2). Moving away from fossil fuels as an energy source/carrier should reduce the amount of CO$_2$ being released into the atmosphere annually, therefore minimizing its contribution to climate change.$^6$

While it is true that greenhouse gases such as CO$_2$ and methane (CH$_4$) are naturally occurring in the atmosphere, with their own natural contributions to global warming (a.k.a. natural radiative forcing), these natural occurring contributions are not considered enough to produce the surface temperature increase Earth is currently experiencing. The increase in greenhouse gas concentration, and the subsequent increase in positive radiative forcing, has long been considered the result of anthropogenic sources. This theory has been tested through the use of the Atmosphere-Ocean General Circulation Models (AOGCM), which are climate models that have been developed from mathematical equations representative of physical law and solved via a three-dimensional grid over the globe. Through the use of such models, in conjunction with instrumentally recorded global mean surface temperatures, researchers have been able to provide evidence that supports this theory. As illustrated in Figure 3,$^6$ the anthropogenic model, which takes into consideration all of the positive radiative forcings from greenhouse gases, surface ozone and aerosols, correlates to the instrumentally recorded data of
Earth’s mean surface temperature increase, while the natural model, that takes into consideration all the natural radiative forcings from solar and volcanic sources, does not. This suggests that the largest contributing factor to the increase in Earth’s surface temperature is in fact from anthropogenic sources. As such, restricting the release of greenhouse gases into the atmosphere could slow the temperature increase that is resulting, in part, from those gases’ positive radiative forcings.
Figure 2 Changes in atmospheric concentrations of carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) over the last 1000 years. Symbols represent ice core and firn (i.e. snow) data collected from Antarctica and Greenland; lines indicate atmospheric data collected over the last several decades. Reproduced with permission from the IPCC Climate Change 2001: The Scientific Basis.⁶
Figure 3 Global mean temperature anomalies relative to the 1880-1920 temperature mean from instrumental record as compared to ocean-atmosphere coupled models with radiative forcings from a) solar and volcanic sources only (i.e. natural sources) b) anthropogenic sources (i.e. well mixed greenhouse gases, changes in stratospheric and tropospheric ozone, and direct and indirect effects of sulfate aerosols) c) both natural and anthropogenic sources (Reproduced with permission from the IPCC Climate Change 2001: The Scientific Basis).
1.3 The Hydrogen Economy

In 2003, the United States’ president George W. Bush and the US Department of Energy (DOE) issued a ‘Grand Challenge’ to the scientific community to partake in the National Hydrogen Storing Project, also referred to as The Hydrogen Economy. The overall purpose of this ‘Grand Challenge’ was to develop an on-board hydrogen storing system that would allow vehicles to operate via a hydrogen fuel cell with little to no noxious emissions (a.k.a. greenhouse gases), as the oxidation of hydrogen (H\textsubscript{2}) produces only water (Equation 1). Use of H\textsubscript{2} from a renewable energy source would be required, however, as the current production of H\textsubscript{2} from steam reforming of methane produces significant greenhouse gas emissions. The ‘Grand Challenge’ was composed of two categories consisting of applied or fundamental research and development: metal/chemical hydrides, carbon-based hydrogen storage materials; and compressed/liquid H\textsubscript{2} technologies, off-board systems, or new materials/technologies.

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \]

**Equation 1** Combustion of hydrogen.

To assure that newly developed technologies would meet at least a light-duty vehicle’s energy requirements, the DOE established a set of targets, the highlights of which are outlined in Table 1. The caveat of these targets is that they are based on the hydrogen storing system in its entirety: tank, material, valves, regulators, piping, mounting brackets, insulation, etc. Often, when reporting hydrogen-storing capacities, researchers only include the gravimetric or volumetric hydrogen-storing capacities of the
energy carrier - not the complete system. This results in hydrogen storing technologies appearing to be better suited to meet our energy needs than they actually are. The only exceptions are compressed and/or cryogenic liquid H₂ tanks, where the complete system is always included. Subsequently, the most advanced on-board hydrogen storing technology in-use consists of 350 and 700 bar compressed H₂ tanks, with hydrogen-storing capacities of 3.4 and 4.7 wt% respectively (system included). These tanks have been used in prototype fuel cell vehicles and are commercially available.¹¹ The gravimetric storage capacities of H₂ tanks approach or exceed the DOE’s 2010 targets, but fall short of the 2017 and Ultimate goals. Regardless, the basis of these new technologies is that H₂ is now serving as an energy carrier, as opposed to the previously used fossil fuels.

**Table 1** Select DOE targets for on-board vehicular hydrogen storage.¹⁰

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>2010</th>
<th>2017</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>System gravimetric density</td>
<td>kg H₂ / kg system</td>
<td>0.045</td>
<td>0.055</td>
<td>0.075</td>
</tr>
<tr>
<td>System volumetric density</td>
<td>kg H₂ / L system</td>
<td>0.028</td>
<td>0.040</td>
<td>0.070</td>
</tr>
<tr>
<td>Durability:</td>
<td>Cycles</td>
<td>1000</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>Charging:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System fill time for 5 kg H₂</td>
<td>kg H₂/min</td>
<td>1.2</td>
<td>1.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

### 1.4 Methods of Hydrogen Production

#### 1.4.1 Reformation

In order for H₂ to be an energy carrier, however, there must also be an energy source. While there are no significant natural H₂ reserves on Earth, due to hydrogen’s low density (0.0899 g/L) allowing it to escape the Earth’s gravity,¹² approximately 50 million
tonnes of H₂ are produced every year for use as a chemical feedstock.¹³ Hydrocarbon reforming is one of the primary industrial sources of H₂ and occurs one of three ways: steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR).¹⁴

Steam reforming (SR) is the process most used in industry. In fact, over 95% of the H₂ produced in the U.S. is generated by steam methane reformation.¹³ SR is an endothermic process that converts hydrocarbons into CO₂ and H₂ in the presence of steam, a supported nickel oxide or precious metal catalyst, temperatures between 600-800 °C, and pressures upwards of 25 bar (Equation 2). The product composition is roughly 3:1 in favor of H₂.¹⁴,¹⁵ The carbon monoxide (CO) generated can then be used to produce more H₂ via the Water-Gas-Shift reaction (Equation 3).

\[
C_mH_n(g) + mH_2O(g) + \Delta \rightarrow mCO(g) + (m + \frac{1}{2}n)H_2(g)
\]

**Equation 2** General overall equation for the steam reformation of hydrocarbons.

The Water-Gas-Shift (WGS) reaction is a two-stage, overall exothermic process: the first stage involves high temperatures (~350 °C) and iron oxide catalysts; the second stage involves lower temperatures (200-300 °C) and copper catalysts. The first stage is necessary to favor fast kinetics, but the increased temperature affects the reaction’s equilibrium position; the CO concentration actually increases. This is why the second stage is necessary: the lower temperature of the second stage decreases the carbon monoxide concentration to less than 1%, with the resultant product mixture being ~ 98% H₂.¹⁴,¹⁵

\[
CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) + \Delta
\]

**Equation 3** The Water-Gas-Shift Reaction.
Partial oxidation reformation (POX) converts hydrocarbons into H\textsubscript{2} via partial oxidation in the presence of oxygen at 1300-1400 °C \textit{without} the use of a catalyst (Equation 4). The energy required to heat the reaction to the necessary operating temperatures is provided by the controlled partial oxidation (i.e. combustion) of the hydrocarbons themselves. The resultant product ratio is 1:1 to 2:1 in favor of H\textsubscript{2}. Following the POX reaction, another WGS reaction takes place to monopolize the CO being formed to produce more H\textsubscript{2}.\textsuperscript{14,15}

\[
C_mH_n + \frac{1}{2}m O_2(g) \rightarrow mCO(g) + \frac{1}{2}n H_2(g) + \Delta
\]

\textbf{Equation 4} The partial oxidation reformation reaction to produce H\textsubscript{2} from hydrocarbons.

Autothermal reformation (ATR) is a combination of these two processes: POX to provide heat energy and SR to increase H\textsubscript{2} production (Equation 5). The WGS reaction can also be used to further refine ATR’s product gas mixture. The result is an overall thermally neutral process that can occur at lower pressures and temperatures than POX (if catalysts are used) and requires no external heat source to drive the reaction (as does SR).\textsuperscript{14,15}

\[
C_mH_n + \frac{1}{2}mH_2O(g) + \frac{1}{4}mO_2(g) \rightarrow mCO(g) + (\frac{1}{2}m + \frac{1}{2} n)H_2(g)
\]

\textbf{Equation 5} The autothermal reformation reaction to produce H\textsubscript{2} from hydrocarbons.

\textbf{1.4.2 Gasification}

Gasification is an exothermic process of producing H\textsubscript{2} from carbon sources such as coal and biomass (Equation 6). The process occurs in a bed reactor (e.g. fixed,
entrained or fluidized), to which steam or oxygen is added to partially oxidize the material; the heat given off by this partial combustion is used to maintain the reaction at the required operating temperature. Entrained bed reactors are often favored for coal gasification because their high operating temperatures ($\geq 1200 ^\circ C$) maximize conversion of carbon to gaseous products (i.e. $H_2$, CO and CO$_2$), and minimize conversion to by-products such as tars, oils and phenols. The product mixture from a bed reactor that uses oxygen (O$_2$) as the oxidant contains between 15-30% $H_2$ and 5-60% CO; if steam is used, the product ratio is 2:1 in favor of $H_2$. Both product streams can be further refined via the WGS reaction to boost $H_2$ production.$^{14,15,16}$

$$C(s) + H_2O(g) + \Delta \rightarrow CO(g) + H_2(g)$$

**Equation 6** General gasification reaction to convert coal into $H_2$.

### 1.4.3 Other Methods

There are a myriad of other methods of $H_2$ production, which, while they will not be discussed in length here, are important to note. These include: $H_2$ from electrolysis (e.g. water, alkaline, polymer electrolyte membrane, etc.), $H_2$ from biomass (e.g. gasification, photolysis or fermentation by algae, etc.), and $H_2$ from reforming (e.g. pyrolysis, plasma reforming, ammonia reforming, etc.).$^{14,16}$
1.5 Methods of Hydrogen Storage

1.5.1 H₂ Compression and Liquefaction

Hydrogen storage by compression involves the use of high-pressure gas cylinders capable of withstanding pressures between 20-70 MPa or higher, depending on the tensile strength of the tank’s material. There are limiting factors to increasing this storage density, however; gravimetric density tends to decrease with increasing pressure due to the requisite increase in tank size and thickness (i.e. weight). The development of new composite tank materials, ones that are lightweight with a tensile strength of 2000 MPa, may increase the gravimetric and volumetric storage densities up to 13 wt% and < 40 kg m⁻³, respectively. The theoretical energy penalty for isothermally compressing H₂ from 0.1 MPa to 80 MPa is 2.21 kWh/kg, however the real energy penalty would be much higher given that the actual compression would not be isothermal.¹⁷,¹⁸

Hydrogen storage by liquefaction occurs via the Joule-Thompson cycle, where H₂ is compressed, cooled, and passed through a throttling valve; this causes the gas to undergo isenthalpic expansion, producing liquid that is cryogenically stored in tanks at 21.2 K. H₂ warms upon expansion however, unlike gases such as N₂, and therefore must be cooled below 202 K (the inversion temperature of H₂) prior to expansion. The gravimetric density of liquid H₂ is system dependent; however the volumetric density is 70.8 kg m⁻³. Due to the low critical temperature of H₂ (33 K), it is necessary for the liquid H₂ to be stored in open systems to avoid the formation of a supercritical fluid. This leads to H₂ losses of 0.06 - 0.4% a day due to boil-off, depending on the tank’s total volume. The heat energy that causes boil-off is, in part, due to the conversion of ortho-hydrogen
to para-hydrogen. Ortho- and para-hydrogen differ by their nuclear spins: for ortho, I = 1; for para, I=0. At room temperature, H₂ is 75% ortho and 25% para; at its normal boiling point (21.2 K), however, H₂ is 0.2% ortho and 99.8% para. This conversion process is exothermic, with a heat of conversion of 523 kJ/kg at 21.2 K; this is greater than the heat of vaporization for normal or para-hydrogen (451.9 kJ/kg) at 21.2 K, and thus the liquid H₂ evaporates and losses occur. The theoretical energy penalty for liquefaction is 3.23 kWh/kg; the actual penalty is much higher at 15.2 kWh/kg.\textsuperscript{17,18}

1.5.2 Physisorption

Physisorption describes the adsorption of an adsorbate (i.e. a gas) onto an adsorbent (i.e. a surface) via Van der Waals interactions. The strength of this interaction is dictated by two competing forces: an attractive force that diminishes with distance at a power of 10\textsuperscript{-6} and a repulsive force that diminishes with distance at a power of 10\textsuperscript{-12}. The consequence of these competing forces is an energy minimum (i.e. binding strength) of 1-10 kJ/mol. The weak nature of the interaction prevents significant physisorption at elevated temperatures (>273 K). Once a monolayer of adsorbate has formed on the adsorbent, additional layers of adsorbate can be ‘deposited’ on top of this monolayer. With multiple layers, however, the interaction is only between adsorbate molecules, and thus the binding strength is dictated by the adsorbate’s heat of vaporization/sublimation. Thus, physisorption occurring at temperatures exceeding the boiling point or sublimation temperature of the adsorbate will only result in monolayer formation. It follows,
therefore, that if the adsorbate is H₂, the hydrogen-storing capacity of the adsorbent is dependent on its surface area, except at very low temperatures (< 21.2 K).\textsuperscript{17,18}

Microporous materials (i.e. pore size < 2 nm), such as carbons, metal-organic frameworks, and some organic polymers, store H₂ via physisorption. The H₂ uptake of these microporous materials can be described by a Type I reversible isotherm, as classified by the International Union of Pure and Applied Chemistry (IUPAC) (Figure 4 IUPAC defined Type I isotherm for physisorption of microporous materials). For a Type I reversible isotherm, filling the adsorbent’s micropores dominates at low pressures, leading to good H₂ uptake; at high pressures, however, a leveling is observed due to the inaccessibility of the remaining pore volume.\textsuperscript{19}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{isotherm}
\caption{IUPAC defined Type I isotherm for physisorption of microporous materials.}
\end{figure}

Carbon nanotubes (CNTs) are a microporous material that consists of hollow graphene rolls. Typically, the diameters of CNTs range between 0.7 nm and several nanometers. A result of such narrow diameters is that the binding force of opposing CNT
walls overlap, increasing the CNT’s ability to bind adsorbate molecules, as compared to flat carbon surfaces; this is why CNTs were originally investigated for H$_2$ storage.$^{18,20}$ In 1997, Dillion et al. reported a CNT hydrogen-storage capacity of 5-10 wt% (not including the system) at room temperature, as determined by thermal desorption performed on a sample consisting of 0.1-0.2 wt% CNT. While this seemed very promising, it was later determined by Hirscher at al. in 2001 that this reported hydrogen-storing capacity was in fact the result of metal nanoparticles that had been deposited during an ultrasonic purification process.

Current research has demonstrated that CNTs still show promise as a hydrogen-storing medium, though often after some modification. In 2012, Aminorroaya-Yamini et al. engineered graphene oxide multiwalled carbon nanotubes (MWCNTs) that stored 2.6 wt% H$_2$ at room temperature under 50 bar. Graphene oxide was the carbon-based material of choice due to theoretical calculations that suggested graphene may be suitable for hydrogen storage, as long as the graphene layers are kept separated and the integrity of their interlayer gaps is maintained (e.g. by oxide formation).$^{21}$ In 2011, Parvin et al. investigated Pd nanoparticle coated MWCNTs and found that the hydrogen-storing capacity increased, relative to undecorated MWCNTs, from 0.3 wt% to 7 wt%, as determined by a volumetric technique under ambient conditions. Palladium was chosen as a dopant due to its prevalence in other H$_2$ related technologies (i.e. fuel cells), and its exceptional ability to chemisorb H$_2$ at volumes roughly 900 times greater than its own.$^{22,23}$
Metal organic frameworks (MOFs) are highly porous, crystalline solids composed of metal ions and organic linkers. MOFs were considered for hydrogen storage due to the immense variability in pore geometry that can result from varying the metal and organic components, thereby increasing their physisorption potential; and for their framework’s exposed metal sites, which can lead to an increase in hydrogen-storing capacity or desorption temperature, by increasing hydrogen-surface interactions. MOFs were also considered due to their demonstrated hysteretic hydrogen storage: the ability to desorb \( \text{H}_2 \) at a higher pressure than it was adsorbed. This has been attributed to the structural flexibility of the MOF’s framework, its ability to stretch and rotate, breath and scissor. One of the prototypical MOFs is MOF-5; it has a three-dimensional cubic lattice composed of zinc oxide (Zn\(_4\)O) clusters at the vertices and 1,4-benzenedicarboxylate linkers along the edges (Figure 5).\(^{20,24}\) Initial investigations suggested that the hydrogen-storing capacity of MOF-5 was 4.5 wt% at 77 K and 0.07 MPa, however these results have been called into question: in 2005, Panella and Hirscher measured a MOF-5 hydrogen-storing capacity of only 1.6 wt% at 77 K and 1 Mpa.\(^{25}\)

Despite this initial discrepancy, research continued on the hydrogen-storing capacity of MOFs. Yaghi et al. reported a 7.5 wt% hydrogen storage for MOF-177 (Zn\(_4\)O(btb) where btb = 1,3,5-benzenetribenzoate) at 77 K and 7.0 MPa, which dropped to 1.25 wt% at 0.1 MPa. Dinca et al. reported a room temperature hydrogen storage capacity of 1.4 wt% at 9.0 MPa for MOF Mn(btt) where btt = 1,3,5-benzenetristetrazolate, with a 77 K hydrogen-storage capacity of 6.9 wt%. More recent research has involved functionalizing MOFs with transition metals (e.g. titanium) and
loading the pores with inorganic hydrides (i.e. NaAlH$_4$),$^{26}$ as well as synthesizing heterometallic MOFs (i.e. Cu$_3$Cr(TSTC)$_2$(H$_2$O)$_4$G, where TSTC = trans-stillbene-3,3’,5,5’-tetracarboxylic acid, and G = guest molecule).$^{27}$ The hydrogen-storing capacities of these newly described MOFs range between 2.7 wt% (at 77 K) and 4.1 wt% (at 473 K).

![Diagram](image.png)

**Figure 5** The cubic lattice of MOF-5. Reproduced with permission from Elsevier.$^{24}$

### 1.5.3 Organic Polymers

Microporous organic polymers have also attracted attention as potential hydrogen-storing materials. The three classes of interest include: polymers of intrinsic microporosity (PIMs); hypercrosslinked polymers (HCPs); and covalent organic
frameworks (COFs). PIMs and HCPs (e.g. cross-linked poly(styrene-co-divinylbenzene) are less structured systems, analogous to activated carbons. Their hydrogen storing capacities are comparatively modest: 2.7 wt% for a triptycene-based PIM (77 K and 1 MPa), and 3.7 wt% for a BCMBP [4,4’-bis(chloromethyl)-1,1’-biphenyl] based HCP (77 K and 1.5 MPa). In addition to their lower hydrogen-storing capacities, PIMs and HCPs are limited in their application due to low thermal stability. COFs, as their name suggests, are organic analogues of MOFs that can achieve impressively high hydrogen-storing capacities: 70-72 mg H₂/ g of material (77 K and 9 MPa). In a 2013 review of prevalent COF technologies, Kalidindi and Fischer highlighted the covalent organic framework COF-12, which is composed of tetra(4-dihydroxyboronylphenyl)methane ligands and boroxine linkages with a ctn topology (Figure 6). The authors reported that COF-12 out performed other COFs with a H₂ uptake of 72.4 mg g⁻¹ (~7.2 wt%) at 77 K.

Maintaining these hydrogen-storing polymers at cryogenic temperatures would likely impede their industrial and/or commercial implementation, however, due to the extra complexities and costs associated with cryogenically cooled systems. Unfortunately, it is likely that increasing the temperature at which these polymers are maintained would only lower their hydrogen-storing density, making them less desirable as a hydrogen-storing technology.
There are several classes of hydrides, including interstitial, simple and complex. Interstitial hydrides, such as PdH$_x$, are formed when metals, or metal containing compounds, react with hydrogen. The metallic element or compound acts as the ‘host’, while the H$_2$ acts as the ‘guest’ molecule. H$_2$ dissociates into atoms on the surface of the metallic host, and diffuses into the interstitial sites of the host’s lattice. The conditions necessary for hydride formation is host dependent. Simple metal hydrides are generally ionic or covalent in nature. Ionic hydrides, such as LiH and NaH, are generally formed by heating the metal under a H$_2$ atmosphere. Covalent metal hydrides, such as MgH$_2$ and AlH$_3$, are formed through a myriad of methods: thermal decomposition of metal containing complexes, reaction of metal salts with other hydride sources, etc. Complex
hydrides, such as NaBH\textsubscript{4} and LiAlH\textsubscript{4}, result from the combination of H\textsubscript{2} with at least two other constituents, typically metallic elements, in fixed proportions. Generally, these hydrides are formed by reacting a simple hydride, comprising one of the metallic constituents, with a compound containing the other, such as a metallic salt.\textsuperscript{29}

Hydrides have been considered for hydrogen-storing applications due to the high gravimetric storage capacities of some (e.g. LiBH\textsubscript{4} at 18.5 wt\%), and the reversible gravimetric capacity of others (e.g. LaNi\textsubscript{5}H\textsubscript{6} at 1.25 wt\%). Hydrides are also of interest due to their ability to form alloys with intermediate properties. Some hydrides are considered too unstable or too stable to be practical for use in hydrogen-storing systems (e.g. simply hydrides); by combining these hydrides however, an alloy, or intermetallic compound of intermediate stability can be formed, increasing said hydride’s potential as a hydrogen-storing system.\textsuperscript{20}

Intermetallic compounds are typically composed of two host materials, components A and B, which form stable and unstable hydrides respectively. The stoichiometry of these H\textsubscript{2} adsorbing compounds vary (i.e. AB\textsubscript{5}, AB\textsubscript{2}, etc.), and only a few form hydrides that are reversible under conditions feasible for hydrogen storage. The model AB\textsubscript{5} intermetallic, LaNi\textsubscript{5}, can form hydrides under moderate temperatures and pressures. One such hydride is LaNi\textsubscript{5}H\textsubscript{6}, which possesses a reversible gravimetric hydrogen-storing capacity of 1.25 wt\%. Unfortunately, LaNi\textsubscript{5}, as well as other AB\textsubscript{5} compounds, are susceptible to disproportionation and can lose their reversibility during cycling; modification of the lattice with Sn (LaNi\textsubscript{5-}xSn\textsubscript{x} where x = 0.2) can reduce this. AB\textsubscript{2} intermetallic compounds can be composed of a myriad of elements, though the A
component typically consists of group 4 metals (i.e. Ti, Zr, etc.) or the lanthanoids (i.e. La, Ce, etc.) and the B component typically consists of any transition or non-transition metal, specifically V, Cr, Mn and Fe. The properties of AB₂ hydrides are host dependent, and can therefore be tuned to the desired application by modifying the composition of the host lattice, as described for AB₅ compounds. Certain AB₂ hydrides can reversibly store H₂, and such hydrides have been used in automotive applications: in the 1980s, Daimler vehicles used the non-stoichiometric AB₂ intermetallic Ti₀.₉₈Zr₀.₀₂Cr₀.₀₅V₀.₄₃Fe₀.₀₉Mn₁.₅ as a hydrogen storing system. The intermetallic system was chosen for its good kinetics and long term cycling stability, however exhibited a fairly low gravimetric density of 1.8 wt%.²⁰

In addition to intermetallic hydrides, there are complex hydrides (vide supra) composed of alkali and alkali earth metals coupled with anionic hydrides (i.e. [AlH₄]⁻ and [BH₄]⁻). In complex hydrides, atomic hydrogen is ionically or covalently bound to the host material and can be released via decomposition of said host material. Complex hydrides composed of [AlH₄]⁻ are referred to as alanates, the model compound of which is sodium alanate, NaAlH₄, which has a gravimetric density of 5.5 wt% (not including the system).³⁰ As sodium alanate dehydrogenates, it initially decomposes into Na₃AlH₆ at 210-220 °C (Equation 7), and then further decomposes into NaH at 250 °C (Equation 8). The dehydrogenation pathways of sodium alanate precluded the possibility of reversibility until Bogdanović and Schwickardi discovered that the addition of TiCl₃ could improve the reaction’s kinetics and reversibility. Other alanates that have been
considered for hydrogen storage include LiAlH\textsubscript{4} and Mg(AlH\textsubscript{4}), which offer hydrogen-storing capacities of 10.5 and 9.3\%, respectively.

\[3\text{NaAlH}_4 + \Delta \rightarrow \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2\]

**Equation 7** The first decomposition step of sodium alanate at 210-220 °C.

\[\text{Na}_3\text{AlH}_6 + \Delta \rightarrow 3\text{NaH} + \text{Al} + 3/2 \text{H}_2\]

**Equation 8** The second decomposition step of sodium alanate at 250 °C.

Complex hydrides containing the [BH\textsubscript{4}]\textsuperscript{-} anion are referred to as borohydrides, of which NaBH\textsubscript{4} and LiBH\textsubscript{4} are the more commonly studied examples.\textsuperscript{31,32} Borohydrides possess some of the highest gravimetric hydrogen-storing capacities of any complex hydride: NaBH\textsubscript{4} and LiBH\textsubscript{4} contain 10.6 and 18.5 wt\% H\textsubscript{2}, respectively. Lithium borohydride thermally decomposes to release H\textsubscript{2} via one of the two following pathways:

\[\text{LiBH}_4 \rightarrow \text{Li} + \text{B} + 2\text{H}_2\]

**Equation 9** Decomposition of LiBH\textsubscript{4} at 730 °C.

\[\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 3/2 \text{H}_2\]

**Equation 10** Decomposition of LiBH\textsubscript{4} at 280 °C.

The decomposition temperature of the first pathway (Equation 9) is too energy intensive to be practical, a consequence of LiH’s stability and resistance to decomposing into Li. The second pathway (Equation 10) does not force the decomposition of LiH into Li, and therefore requires less energy; however, less stored H\textsubscript{2} is released. The
dehydrogenation of LiBH₄ is a reversible process, however re-hydrogenating it requires very high temperatures and pressures to be successful: 20-35 MPa and 600-700 °C.

Sodium borohydride can release H₂ under ambient conditions through hydrolysis (Equation 11). There is a significant energy barrier to borohydride regeneration after hydrolysis, however; this is a consequence of the stability of the [BO₂]⁻ species. There is also the added complication of transporting the hydrolyzing material with NaBH₄ to affect H₂ release and solvate the borate (NaBO₂) by-product; this added weight dramatically decreases the gravimetric H₂ density of the system from 10.8 wt% to 5.5 wt%. An alternative, which offers several advantages over hydrolysis, is methanolysis. While the gravimetric H₂ density for methanolysis is only 4.9 wt%, it offers rapid, uncatalyzed H₂ evolution from NaBH₄ at subzero temperatures (melting point of methanol: -98 °C). In contrast, hydrolysis is slow without the presence of a catalyst, and is limited to operating temperatures above 0 °C.

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2
\]

Equation 11 Hydrolysis of NaBH₄ under ambient conditions.

\[
\text{NaBH}_4 + 4\text{CH}_3\text{OH} \rightarrow \text{NaB(OCH}_3)_4 + 4\text{H}_2
\]

Equation 12 Methanolysis of NaBH₄ under ambient conditions.

The presence of water during NaBH₄ methanolysis is known to significantly reduce the rate of H₂ evolution, however. Consequently, Huynh et al. investigated the methanolysis of NaBH₄ under rigorously dry conditions. The authors determined the concentration of NaBH₄ in methanol that was necessary to maintain its rate of H₂
evolution. They reported that the best rates were achieved with 40 molar equivalents of rigorously dried methanol relative to NaBH$_4$.

1.6 Hydrogen applications

Once H$_2$ has been successfully manufactured and stored, it can then be used to do work. Two of the systems available to accomplish this are H$_2$ fuel cells and internal combustion engines.

1.6.1 Fuel cells

Fuel cells are systems that convert chemical energy into electrical energy. The electrical energy, once generated, can then be used to do work. There are many different types of fuel cells (Table 2), each with its own set of advantages and disadvantageous; one of the more ubiquitous types is the polymer electrolyte membrane (PEM) fuel cell. The choice of fuel cell is system dependent: what the system’s processes entail, and what their energy requirements are. As outlined in Table 2, PEM fuel cells are often utilized for vehicular or portable power applications.
### Table 2 Comparison of available fuel cell systems.\(^{35}\)

<table>
<thead>
<tr>
<th>Fuel cell</th>
<th>Electrolyte</th>
<th>Operating temperature (°C)</th>
<th>Efficiency (%)</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer electrolyte membrane (PEM)</td>
<td>Typically perfluorosulfonic acid</td>
<td>Typically 80</td>
<td>35-60</td>
<td>Portable power/Transportation/specialty vehicles</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>Matrix loaded with KOH(_{\text{aq}})</td>
<td>90-100</td>
<td>60</td>
<td>Military/space</td>
</tr>
<tr>
<td>Phosphoric acid (PAFC)</td>
<td>Matrix loaded with H(_2)PO(_4)</td>
<td>150-200</td>
<td>40</td>
<td>Distributed generation</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>Matrix loaded with solution of alkali metal carbonates</td>
<td>600-700</td>
<td>60</td>
<td>Electric utility/Distributed generation</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>Yttria-stabilized zirconia</td>
<td>700-1000</td>
<td>60</td>
<td>Auxiliary power/Electric utility/Distributed generation</td>
</tr>
</tbody>
</table>

The working component of a standard PEM fuel cell is the membrane electrode assembly (MEA) (Figure 7). The MEA is comprised of two electrodes, the anode and the cathode, and a polymer electrolyte. The electrodes typically consist of Pt/C affixed to an electrically conductive, porous carbon cloth. The cloth acts as a gas diffusion layer, which diffuses the fuel and oxidant gases onto the electrodes, forms an electrical connection between the electrode and outer circuit, and in the case of a H\(_2\) fuel cell, carries the water produced away from the MEA (Figure 8). The polymer electrolyte is typically comprised of acid-functionalized polytetrafluoroethylene (PTFE); the industrial
standard for PEM fuel cell membranes is Nafion®, a perfluorosulfonic acid PTFE copolymer (Figure 9).34

![ PEM fuel cell assembly complete with membrane electrode assembly (MEA) (Reproduced with permission from Mark Skerritt)](image)

**Figure 7** PEM fuel cell assembly complete with membrane electrode assembly (MEA) (Reproduced with permission from Mark Skerritt)39

![ Fuel cell MEA showing oxidation and reduction reactions.](image)

**Figure 8** Fuel cell MEA showing oxidation and reduction reactions.
In a standard H\textsubscript{2} PEM fuel cell, H\textsubscript{2} is oxidized at the anode via the following half reaction (Equation 13):

\[ 2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^- \]

\[ E^\circ = 0.0 \text{ V by definition} \]

**Equation 13** Oxidation half reaction at a fuel cell's anode.

Due to the inherent electrical insulating properties of the PEM, the electrons travel from the anode to the cathode through an external circuit, which can be load bearing. The protons migrate through the polymer electrolyte, which separates the electrodes, via the Grotthuss mechanism. The electrons and protons recombine at the cathode in the presence of O\textsubscript{2} to form water (Equation 14). Consequently, the open circuit voltage
(OCV) for such a H₂ PEM fuel cell is 1.23 V, the theoretical maximum potential that the fuel cell can provide.

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \\
E^\circ = 1.23 \text{ V}
\]

**Equation 14** Reduction half reaction at the fuel cell's cathode.

The Grotthuss mechanism was proposed by von Grotthuss in 1806, and is otherwise referred to as the proton ‘hopping’ mechanism. The Grotthuss mechanism relies on the H-bonding network of water to move protons across a series of H⁺ acceptors. Consequently, a PEM fuel cell must be properly hydrated in order to maintain function: it is the solvated, sulfonated side chains of the Nafion® membrane that shuttle the protons from the anode to the cathode (Figure 10).

While the electrical output from each fuel cell may be small (OCV = 1.23 V), a significant voltage can be produced by arranging fuel cells in series. This is accomplished by connecting the cathode of one fuel cell to the anode of the other, in succession. Arranged in this manner, the voltage each fuel cell provides is additive. Comparatively, a significant current can be produced by arranging fuel cells in parallel. The arrangement of multiple fuel cells, in series or in parallel, is referred to as a fuel cell stack. The number of fuel cells in a stack, and the number of stacks in a system, is dependent on the amount of electrical energy that is required to meet the energy demands of the system (e.g. powering a vehicle). In 2010, the world’s largest demonstration fleet of 20 fuel cell electric transit buses was implemented in British Columbia; each bus was powered by 150 kW fuel cell module.
Figure 10 Grotthuss mechanism in the context of proton transfer in a PEM fuel cell.

1.6.2 H₂ Internal Combustion Engine

A H₂ internal combustion engine (ICE) is simply a conventional ICE that has been modified to burn pure H₂, or a H₂-natural gas blend, instead of gasoline. H₂ ICEs can offer upwards of 25% more fuel efficiency than conventional engines, while producing near-zero carbonaceous or noxious emissions. They are considered less efficient than a fuel cell powered vehicle, which can travel farther per unit of H₂; however, the relative simplicity and cost efficiency of the H₂ ICEs could make them easier to implement in the long term. H₂ ICEs reportedly perform well under any and all weather conditions, requiring no warm-up, and, even at sub-zero temperatures, do not
suffer from cold-start issues. A major disadvantage of the H\textsubscript{2} ICE, however, is the current lack of H\textsubscript{2} refueling infrastructure. The necessary size of the H\textsubscript{2} storage tanks also compromises cargo space, which may make a H\textsubscript{2} ICE-powered vehicle less attractive to consumers.\textsuperscript{42,43}

Despite these challenges, the Ford Motor Company launched a series of H\textsubscript{2} ICE powered shuttle buses and cars in Canada, as part of an important pilot program.\textsuperscript{44} The information gathered has helped establish the stability and durability limits of a H\textsubscript{2} ICE system, and help establish the international codes and standards necessary to build a market for H\textsubscript{2} ICE-powered vehicles.

1.7 Catalysis

An understated necessity to the successful implementation of the Hydrogen Economy is catalysis. Catalysis plays a critical role in H\textsubscript{2} production, storage, and application: it makes these processes possible on a time-scale that is useful to us as human beings. Subsequently, the following sections will focus on concepts pertaining to the type of catalysis that is prevalent in the Hydrogen Economy and the contents of this thesis: heterogeneous catalysis.

1.7.1 The Basics of catalysis

The outcome of any chemical reaction can be explained through the principles of thermodynamics and kinetics (Figure 11). Fundamentally speaking, the principles of thermodynamics encompass the energy difference between reactants and products,
defined as the change in Gibbs free energy ($\Delta G$), and the implications of said energy difference on the reaction (e.g. product distribution, equilibrium position, reaction spontaneity, exo/endothermicity, etc.). The principles of kinetics encompass the energy difference between reactants and the transition state, defined as the Gibbs free energy of activation ($\Delta G^\ddagger$), and the implications of that energy difference on the reaction (e.g. reaction rate, product distribution, etc.). Chemists can use these principles to manipulate and/or design reactions to produce a specific product at a desirable rate. One of the ways chemists can accomplish this is through catalysis.

Catalysis is the process through which a catalyst increases the rate of a reaction without influencing its overall change in Gibbs free energy. Theoretically, a catalyst is neither produced nor destroyed during a reaction, though in practice both can occur. There are two main classes of catalysts: heterogeneous and homogeneous. Homogeneous catalysis is molecular in nature, comprising the discreet catalytically active sites of individual molecules functioning in solution. Heterogeneous catalysis is atomic in nature, comprising large agglomerations of metal or metal oxide atoms and their manifold of catalytically active sites, functioning at an interface.\textsuperscript{45} The IUPAC defines homogeneous catalysis as occurring in one phase; whereas heterogeneous catalysis is defined as occurring at or near the interface of two phases.\textsuperscript{46,47} In practice, however, there are exceptions to both of these fundamental definitions: homogeneous catalysis can occur at an interface, wherein the catalyst is dissolved in one phase and the reactant(s) is dissolved in a second phase;\textsuperscript{48} heterogeneous catalysis can be accomplished with homogeneous catalysts immobilized on a solid support.\textsuperscript{49}
There are advantages and disadvantages to both types of catalysis. A homogeneous catalyst can be intelligently designed, by careful selection of the ligands around its metal center, to selectively catalyze one reaction pathway over another for a particular synthesis (Figure 12);\textsuperscript{50} they can also offer great selectivity and reproducibility of results under mild conditions. Homogeneous catalysts are often more expensive, however, due in part to the cost of their ligands; and catalyst isolation/recyclability is often complicated by the fact that the catalyst and reaction mixture are in one phase. Comparatively, heterogeneous catalysts also offer high selectivity,\textsuperscript{51} but with the added benefit of catalytic robustness and ready isolation from reaction mixtures; this increases...
the catalysts’ capacity to be continuously recycled. Heterogeneous catalysts are used most ubiquitously in industrial processes.\textsuperscript{45}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{catalyst.png}
\caption{Example of a homogeneous catalyst designed for hydroformylation.\textsuperscript{50}}
\end{figure}

1.7.2 Surfaces of heterogeneous catalysts

As previously described, heterogeneous catalysis occurs at the interface between a catalyst’s surface and the reaction mixture. Thus, to better understand the heterogeneous catalytic process, it is necessary to understand the catalyst’s surface. The transition metals, which encompass the majority of the catalytically active elements, exist in three different lattice structures: face centered cubic (fcc), body centered cubic (bcc) and hexagonal close packing (hcp) (Figure 13). The text herein will focus on the face centered cubic lattice, and its surfaces.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{lattices.png}
\caption{The unit cell for fcc, bcc, and hcp lattices (Reproduced with permission from Dr. Philip Jessop).}
\end{figure}
The fcc transition metals include Pd, Pt, Rh, Ir, Au, Ag, and Ni, which are among the mostly catalytically active and widely used metals in heterogeneous catalysis.\textsuperscript{52–54} The fcc lattice follows the ABCABC packing sequence (Figure 14), wherein the A layer of atoms is situated in a close packed hexagonal arrangement. The B layer of atoms sits within the inter-atomic hollows of the A layer, while the C layer of atoms sits within the inter-atomic hollows of the B layer, offset from the other two layers. After this third layer, the sequence repeats itself. The result of this packing structure is that the atoms are as closely packed as possible, each with a coordination number of 12.

\textbf{Figure 14} The ABCABC packing sequence of the fcc lattice. The orange-labeled atoms on the right are smaller to emphasize their position relative to the other atoms (Reproduced with permission from Dr. Philip Jessop).

The fcc lattice and ABCABC packing sequence best define the bulk metallic structure; however, some of the most catalytically active surfaces result from the bulk metallic structure being ‘cut’ along planes to reveal the atoms below. To define these planes and the atomic structures they reveal, chemists implemented the Miller indices. These indices are used to name and define specific catalytic surfaces, or \textit{faces}. 
To invoke the Miller indices, a unit cell is situated along x, y, and z axes. With respect to the fcc unit cell, ‘cutting’ along the plane perpendicular to the x-axis at (1, 0, 0) reveals the (100) face (Figure 15). In other words, the (100) face is perpendicular to the (100) vector from the origin. The (110) and (111) face of the fcc lattice can be revealed by ‘cutting’ the unit cell perpendicular to the (1, 1, 0) and (1, 1, 1) vector, respectively (Figure 16). Each of these fcc faces has a positive energy of formation associated with them given that the bulk material has to be ‘cut’, and bonds have to be broken, in order for these faces to form. That being said, not all of the surfaces are created equally.

**Figure 15** Miller indices: fcc (100) face (Reproduced with permission from Dr. Philip Jessop).
A stable catalytic surface requires a high density of surface atoms, each with a high coordination number. In terms of the fcc lattice, face stabilities are as follows: (111) > (100) > (110). This trend in stability can be explained by coordination numbers (CN): each surface atom of the (100) face has a CN of 8 (four atoms in the plane, and four below it); each surface atom of the (110) face has a CN of 7 (two atoms in the plane, four below the plane, and one atom below the second plane); and each surface atom of the (111) face has a CN of 9 (six atoms in the plane, and three below it). The least stable of these faces can, and often do, undergo surface reconstruction to minimize their higher surface energies. These reconstructions can include perpendicular and parallel restructuring, as well as array changes. In perpendicular restructuring, the spacing between the surface layer of atoms and the atomic layer beneath it decreases relative to
the bulk crystal. In parallel restructuring, the surface layer of atoms moves parallel to the atomic layer beneath it, offsetting the layers from their original positions (Figure 17). Array changes entail, for example, the reconstruction of a (100) square array into a (111) hexagonal array. It is not always apparent, however, why certain surface reconstructions actually minimize surface energies.\textsuperscript{55}

In addition to reconstructions, defects can occur on a catalyst’s surface: holes/vacancies, adatoms, islands, steps, and kinks (Figure 18). There are a myriad of causes for such defects: surface restructuring, synthetic methodologies, synthetic applications, etc. As with lattice faces, defects can vary in surface energy due to their lower coordination number relative to the bulk crystal. Consequently, if defects act as catalytically active sites during a reaction, they can strongly influence a catalyst’s overall activity and selectivity.

Figure 17 Surface reconstructions: Perpendicular (A) and Parallel (B) restructuring.
1.7.3 General mechanism of heterogeneous catalysis

Whether it occurs on a (111) face or a surface kink, a reaction being catalyzed on the surface of a heterogeneous catalyst has multiple mechanistic steps associated with it. Consider, for example, the general mechanism for the hydrogenation of an alkene. The first step in the mechanism involves the diffusion of the reagents to the surface of the catalyst (Figure 19):

Figure 19 Diffusion and adsorption of reactants on the catalyst's surface.

This step is followed by the migration and reaction of the adsorbed species on the surface of the metal (Figure 20):
Figure 20 Surface migration and reaction of adsorbed species.

After formation, the product desorbs from the catalyst’s surface and diffuses away.

1.7.4 Kinetics of heterogeneous catalysis

While the general mechanistic steps of a heterogeneous catalyzed reaction are known, it can be difficult to define the rate-determining step. Two generally accepted methods of describing heterogeneous catalyzed reactions and expressing their rate-determining steps include the Langmuir-Hinshelwood mechanism, and the Eley-Rideal mechanism. Each proposed mechanism has its own set of kinetic expressions associated with it, which are defined by what is involved in the reaction’s rate determining step (RDS). Generally, Langmuir-Hinshelwood kinetics describe the reaction of two species adsorbed onto the surface of a catalyst: it is assumed that all adsorption and desorption processes are in equilibrium with the gas phase, and that the RDS is the surface reaction between the adsorbed species. In turn, Eley-Rideal kinetics generally describes the reaction between two species, wherein one species, strongly adsorbed to the catalyst surface, reacts with another species that approaches from the gas phase (Figure 21). The specifics of Langmuir-Hinshelwood kinetics will be described herein.\(^{57}\)
Figure 21 The Langmuir-Hinshelwood and Eley-Rideal mechanisms, wherein A and B are reagents and C is the product.¹⁸

Langmuir-Hinshelwood kinetics are based upon the Langmuir isotherm, which depicts the reversible adsorption of a gas onto the surface of a metal:

\[ A_{(g)} \rightleftharpoons A_{(ads)} \]

Since the adsorption is in equilibrium, the rate of adsorption (a) is equal to the rate of desorption (d), therefore:

\[ k_a P_A (1-\theta_A) = k_d (\theta_A) \]

\[ k_a/k_d = P_A (1-\theta_A) = (\theta_A) \]

\[ b_A = k_a/k_d \]
where: \( k = \) rate constant, \( P_A = \) pressure of A, \( (1-\theta_A) = \) sites not covered by A, \( \theta_A = \) the surface coverage of A

Rearranging for \( \theta_A \) gives:

\[
\theta_A = \frac{b_A P_A}{1 + b_A P_A}
\]

For the bimolecular reaction:

\[
A_{(g)} + B_{(g)} \rightarrow C_{(g)}
\]

where two adsorbed species exist on the surface of the catalyst, then surface coverage with respect to both species is expressed as:

\[
\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B + b_C P_C}
\]

\[
\theta_B = \frac{b_B P_B}{1 + b_A P_A + b_B P_B + b_C P_C}
\]

Subsequently, the rate law for said bimolecular reaction can be expressed as:

\[
\text{rate} = k \theta_A \theta_B
\]

\[
\text{rate} = k \frac{b_A P_A b_B P_B}{(1 + b_A P_A + b_B P_B + b_C P_C)^2}
\]

For the unimolecular reaction:

\[
A_{(g)} \leftrightarrow B_{(g)} + C_{(g)}
\]

where one adsorbed species reversibly reacts to produce two adsorbed species, such as in a dehydrogenation reaction, the rate law expression must account for the vacant site, \( \theta_V \),
that product \( C_{(g)} \) will occupy when the surface reaction is complete. Site vacancies for a reversible unimolecular reaction leading to two adsorbed products are expressed as:

\[
\theta_v = \frac{1}{1 + b_A P_A + b_B P_B + b_C P_C}
\]

As such, the rate law can be expressed as:

\[
\text{rate} = k_1 \theta_A \theta_v - k_{-1} \theta_B \theta_C
\]

\[
\text{rate} = (k_1 b_A P_A - k_{-1} b_B P_B b_C P_C) / (1 + b_A P_A + b_B P_B + b_C P_C)^2
\]

1.7.5 Preparation of supported heterogeneous catalysts

The crux of heterogeneous catalysis is that reactions occur on a surface (e.g. the surface of a metal or metal oxide); typically, the greater the surface area, the faster the reaction. Consequently, the distribution of fine metal particles on a solid support is favored over the use of bulk metal. The options for synthesizing such finely distributed, supported catalysts are wide and varied, and the subject of numerous books and articles.\(^{59}\)

The text herein will focus on two such methods: sol-gel and wet impregnation methods.

The term sol-gel derives its name from the word ‘sol’, which describes a colloidal suspension of small solid particles in liquid (1 nm to 1 µm); and ‘gel’, which describes continuous solid and liquid phases of colloidal dimensions. In the context of catalyst synthesis, however, it refers to the formation of a gel from a homogeneous solution of support and metal precursors. The support precursor most commonly used is a metal
alkoxide, M(OR)$_x$, where M = Si, Al, Ti, etc., and R = CH$_3$, CH$_2$CH$_3$, etc. Metal alkoxides are the support precursor of choice due to their penchant to hydrolyze into metal hydroxides (M(OH)$_x$), which can then undergo condensation polymerizations to form the metal oxide support. The metal precursor can be any available salt, although typically it’s a metal chloride or metal acetate salt. Once polymerization of the metal alkoxide is induced, the metal precursor deposits and becomes widely dispersed throughout the polymeric support as it takes shape. The newly formed catalyst must then be dried and calcined before use. The result is a unique morphology that is generally not observed for more traditional methods of catalyst preparation, such as wet impregnation.$^{56}$

Impregnation is based on the expectation that suspended metal particles will physically adsorb onto the surface of a support, or interact with the surface hydroxyl groups of the support, if metal salt precursors are used. There are two general types of impregnation: dry and wet. In dry impregnation, the amount of metal-containing solution is less than or equal to the pore volume of the support. This method depends on retaining the metal species within the pores of the support, instead of monopolizing on any specific interaction with the support (e.g. reacting with surface hydroxyl groups). Consequently, dry impregnation can make it easier to control how much metal is actually deposited onto the surface of the support. Wet impregnation entails using a solution volume greater than the pore volume of the support. As a result, the metal or metal precursor becomes well dispersed throughout the support. There is a risk, however, if the metal concentration is too low, that the metal will be taken up almost exclusively at the mouth of the pores,
forming an ‘egg shell catalyst’ that may or may not be desired. In both dry and wet impregnation, the drying step is of particular importance: if the catalyst’s drying process is carried out too quickly, liquid contained in the pores may be forcefully driven out by vapor forming within the pores, resulting in the deposition of metal or metal precursors on the surface of the support that is not strongly adsorbed.59

1.7.6 Support and modifier effects

It has been reported that the careful selection of a heterogeneous catalyst’s support can affect its activity and selectivity. This phenomenon has been referred to as the ‘support effect’, and is attributed, in part, to the acid-base properties of the supports themselves. It is expected that the electronic nature of the metal is affected due to the electron donating and withdrawing properties of basic and acidic supports, respectively.

The support effect is best exemplified in the literature. In 2003, Niwa et al. investigated the combustion of toluene over Pd supported on various metal oxides: MgO, Al₂O₃, SiO₂, SnO₂, Nb₂O₅, WO₃ and ZrO₂. They reported that the most active Pd catalysts were supported on weakly acidic or basic metal oxides, such as Al₂O₃, SiO₂, SnO₂, and Nb₂O₅. The Pd catalysts supported on strongly acidic or basic metal oxides, such as WO₃ and MgO, were essentially inactive. The authors reported that there was no apparent correlation between catalytic activity and catalytic surface area or metal distribution; thus all differences were attributed to the supports. Niwa et al. also investigated the ease of PdO formation relative to the support. They found that acidic
supports enabled PdO formation; their electron-withdrawing nature rendered Pd electron deficient. Conversely, basic supports hindered PdO formation due to their electron donating nature. The authors suggested that this penchant for PdO formation, or lack thereof, may have optimized their Pd catalysts towards toluene combustion when weakly acidic or basic supports were used.\textsuperscript{60}

A heterogeneous catalyst’s support can also partake in catalysis. Hydrogen spillover is a phenomenon where molecular hydrogen dissociates on a catalyst’s surface and migrates to the catalyst’s support. This phenomenon is sometimes looked upon as a means of hydrogen storage,\textsuperscript{20} but can also influence reactions being catalyzed on the metal surface. In 1993, Srinivas and Rao reported the influence of H\textsubscript{2} spillover in the hydrogenation of benzene over Pt/C.\textsuperscript{61} It was reported that contamination of the Pt surface with carbon provided the bridges necessary for adsorbed H atoms to spillover onto the support itself. Subsequently, the authors diluted Pt/C with more carbon and found that H\textsubscript{2} spillover was occurring in their system at room temperature. Their data suggested that, not only was benzene being hydrogenated on the Pt surface, it was also being hydrogenated on the carbon diluent due to H\textsubscript{2} spillover.

A heterogeneous catalyst’s activity can be influenced not only by supports, but also by modifiers. There are two classes of modifiers: promoters and poisons. Promoters are often electropositive elements, such as the alkali metals. They work by activating the metal sites around them, but are not catalytically active themselves; they increase the binding strength of reactants on the metal’s surface, and lower the desorption energy of the products. Promoters preferentially situate themselves at the surface of the catalyst,
and tend not to be incorporated into the bulk crystal. A quintessential example of promoters in catalysis is the role of potassium in the synthesis of ammonia. In the early 1900s, Fritz Haber discovered that N₂ and H₂ react over magnetite (Fe₃O₄) to produce ammonia. It was later established, however, that the magnetite had to contain potassium oxide impurities in order to properly catalyze the reaction; pure magnetite was catalytically inactive. In contrast, poisons are often electronegative elements, such as halides and sulfur containing compounds; they work by deactivating the metal sites around them. A poison’s strength depends on its placement in the metal lattice: they are stronger if they have been incorporated into the surface layer of metal atoms, versus simply adsorbing onto the catalyst’s surface. Poisons can be quite advantageous, however; in certain circumstances, they offer increases in selectivity. In 2010, Medlin et al. reported the use of alkyl thiols as dopants: in the presence of Pd/Al₂O₃, the alkyl thiols formed self-assembled monolayers on the catalyst’s (111) surfaces. The resultant catalysts afforded selectivities of 80-94% for the hydrogenation of 1-epoxy-3-butene to 1-epoxybutane; traditional catalysts only offered upwards of 11%. The authors did report a decrease in conversion relative to the untreated catalysts; however, given the nature of poisons, the observed deactivation is not unreasonable.

1.7.7 Characterization of heterogeneous catalysts

Characterizing a heterogeneous catalyst is generally less straightforward than characterizing a homogeneous catalyst. The structure of a homogeneous catalyst can be probed by more traditional techniques such as infrared and nuclear magnetic resonance
spectroscopy; for a heterogeneous catalyst, such techniques are generally less effective for elucidating structural information. Despite the challenges, however, it is still important to gain understanding of a heterogeneous catalyst’s surface area and structure. This can be accomplished by a number of techniques, of which two will be discussed here: the Brunauer, Emmett, and Teller (BET) theory for surface area determination, and transmission electron microscopy for structural elucidation.

The BET theory was developed to describe the adsorption of species onto surfaces. It is similar to the Langmuir isotherm (Section 1.7.4), which describes the adsorption of a monolayer onto a surface. The way in which BET theory differs, however, is that it allows for multiple adsorbent layers to form before a surface is completely covered by a monolayer. The BET theory is best described by the following equation:

$$V_{ads} = V_m c P / (P_o - P)[1 + (c - 1)P/P_o]$$

Equation 15 BET equation for surface coverage where: $V_{ads}$ is the volume of gas adsorbed, $V_m$ is the volume required to give a monolayer of adsorbed molecules, $P$ is the measured pressure of the gas, $P_o$ is the saturated vapor pressure of the gas at the adsorption temperature, and $c$ is a fitting constant.

This expression can be linearized as:

$$P / [V_{ads}(P_o - P)] = (1/V_m) + [(c - 1)P / V_m] x P_o$$

Equation 16 Linearized BET equation.

Consequently, a plot of $P / [V_{ads} (P_o - P)]$ versus $P / P_o$ will have a y-intercept of $1 / V_m c$ and a slope of $(c - 1) / V_m c$. From these expressions, $V_m$ can be calculated, and by extension,
so can the surface area (Equation 17).\textsuperscript{64} Thus, under conditions necessary for monolayer formation, BET theory can be utilized to determine the surface area of a heterogeneous catalyst.

\[
S = \frac{V_m N_a}{(m \times 22400)}
\]

**Equation 17** Specific surface area expression, where \(V_m\) is the volume required to form a monolayer of adsorbed molecules; \(N_a\) is Avogadro’s number; and \(m\) is the mass of the sample.

While BET theory can be used to establish surface area, transmission electron microscopy (TEM) can be used to structurally elucidate heterogeneous catalysts. As the name suggests, TEM is a form of microscopy; it allows researchers to actually see the metal nanoparticles and solid supports that comprise a heterogeneous catalyst. As such, the size, morphology and distribution of metal nanoparticles on a support can be characterized. To produce images on a nano-scale, TEMs use a beam of high-energy electrons (100-400 keV) to focus on the sample, in a way that is analogous to a traditional light microscope. The use of electrons over electromagnetic radiation allows for significantly higher magnifications (2000 – 200 000x). To analyze a sample by TEM, it must first be suspended in a solvent and deposited on a copper or gold grid, which is typically coated in carbon or a polymer film. The sample-bearing grid is then placed in a high vacuum chamber; once the electron beam is focused on the grid, acquisition of sample images can begin.\textsuperscript{65}
1.8 Overarching objective

The overarching objective addressed by this body of work entails the preliminary development of select hydrogen-storing technologies for vehicular application. Two distinctively different technologies were investigated: a hydrogen-storing siloxane polymer, and a thermally regenerative fuel cell system. Both technologies will be discussed, at length, in the chapters that follow. The motivation behind the development of these technologies was the deceleration of non-renewable resource depletion (e.g. fossil fuels), and the reduction of anthropogenic carbon dioxide emissions.
1.9 References


(58) Nanyang Technological University Chapter 3: Kinetics Adsorption vs Activity.
Chapter 2

Towards a Thermally Regenerative Fuel Cell System

2.1 Introduction

A thermally regenerative fuel cell (TRFC) system, in general terms, turns heat into electricity.\textsuperscript{1,2} We have proposed a TRFC system that would convert the waste heat energy from an internal combustion engine (ICE) system (i.e. engine, catalytic converter, exhaust, etc.), into electricity that could charge a battery to power auxiliary vehicular components (e.g. lights, radio, cooling/heating systems, charging hybrid vehicle batteries, etc.), thereby supplementing or supplanting a vehicle’s alternator. Our TRFC system was developed in response to the inefficiency of current ICE systems. The overall efficiency of a typical diesel-powered ICE is between 37-45 \% of the total energy input from fuel, with the remaining energy lost as waste heat.\textsuperscript{3} Implementation of our TRFC system into such ICE systems could improve that efficiency by several percent. As such, we have proposed that one application of our TRFC system is implementation in long haul trucking vehicles, where small increases in fuel efficiency could have a relatively large impact on diesel consumption, per trucking company.

2.1.1 Established precedent for TRFC systems

There is precedence for TRFC systems in the literature. In a 1965 symposium on regenerative EMF cells, J. Angus reported a TRFC system involving I\textsubscript{2}/PbI\textsubscript{2} as a
continuous gas concentration cell.\textsuperscript{4} Iodine, held in a high-pressure reservoir, absorbed thermal energy at temperatures $\leq 400\, ^\circ\text{C}$, vaporized, and diffused through a PbI$_2$ electrolyte. A potential difference was generated from the electrochemical expansion of I$_2$ through the electrolyte causing a concentration gradient. The I$_2$ then condensed in a low-pressure reservoir, allowing the system to be regenerated by applying heat to that reservoir. The purported advantage of this system is the absence of any chemical reaction; no chemical regeneration or separation step was required. The toxicity of the materials used,\textsuperscript{5,6} however, and the necessity to operate at high temperatures are undesirable. While no application was outlined for this TRFC system, it can be inferred from the other symposium publications that it was potentially intended for use in the space program.

Ando et al.\textsuperscript{2} have offered a more recent example of a TRFC system, one involving an organic liquid that acts as the hydrogen source for a PEM fuel cell. In this system, aqueous isopropanol is supplied to the fuel cell’s anode, maintained at $80\, ^\circ\text{C}$ by a low temperature heat source, where the isopropanol dehydrogenates into acetone and H$_2$. The H$_2$ splits into electrons and protons that travel through an outer circuit and a Nafion® proton exchange membrane (PEM), respectively, to produce electricity. At the cathode, maintained at $25\, ^\circ\text{C}$, the acetone, protons and electrons combine to regenerate isopropanol; and thus the cycle continues. The use of aqueous isopropanol was necessary due to the incorporation of Nafion® into the PEM fuel cell. Nafion® must maintain an appropriate hydration level in order to function properly. Initial currents and voltages obtained from the system were very low: $< 6\, \text{mA}$ and $\leq 20\, \text{mV}$, respectively.
Optimization of the cathode catalyst and electrolyte system increased the current and voltage, but only to 50-100 mA and 100 mV respectively. Furthermore, isopropanol has a limited temperature range over which it can operate, thus limiting the TRFC’s ability to convert waste heat to electricity directly. The proposed application for this TRFC system, however, was to convert low temperature thermal energy, such as solar thermal energy, into electricity, and so isopropanol is appropriate for this application.

In 2007, Akimoto proposed another isopropanol based TRFC system. In Akimoto’s system, however, the dehydrogenation of isopropanol occurs in the gas phase within a heated chamber. The H₂ produced is separated from the dehydrogenated product, acetone, by a separation unit that sends the H₂ to a PEM fuel cell and the acetone to a hydrogenation chamber. The PEM fuel cell acts as a gas concentration cell, where the concentration difference of H₂ across the electrodes generates a potential difference, creating an electrical current. As such, the H₂ is split into protons and electrons at the anode, and recombine to form H₂ at cathode. Once reformed, the H₂ is sent to the hydrogenation chamber, via a gas compressor, to hydrogenate acetone back to isopropanol, so that the system may continue to cycle. There are challenges involved in working with such a gas-phase TRFC system: the low density of reactant molecules would require a high catalyst loading to ensure reasonable reaction rates; and the requirement of a separation unit, and gas compressor, to isolate and move H₂ throughout the system adds structural complexity and increased energy consumption. One advantage, however, is that the PEM is never exposed to the TRFC’s organic components, isopropanol and acetone, which precludes any possible incompatibilities and subsequent
complications. An application for this TRFC system could not be deduced from the patent describing the invention; however, it could be inferred, due to the gas-phase nature of the TRFC system, that it was designed to convert low to moderate thermal energy into electricity.

2.1.2 Project’s premise

Our proposed TRFC system (Figure 22) involves a dehydrogenation reactor and a fuel cell that would be positioned relative to a heat source (i.e. a component of an ICE system) such that the reactor is held at 200 °C and the fuel cell is held at 100 °C. A hydrogen storing liquid (XH₂) would be passed through the reactor where it would dehydrogenate in the presence of a heterogeneous catalyst to give the dehydrogenated liquid (X) and H₂. The H₂ would be sent to the fuel cell’s anode, while X would be sent to the cathode of the fuel cell where it would serve as the oxidant. With the introduction of both species at the fuel cell, electricity would be produced. At the cathode, protons, electrons and X would recombine to form the working fluid, XH₂. This liquid would then be sent back to the reactor, allowing the system to continuously cycle. Consequently, the TRFC system would be maintained as a closed system to facilitate the cycling of reactive materials, and, for the sake of safety and practicality, it would be maintained under nearly ambient pressure of H₂.
To ensure that our TRFC system operates with highest possible efficiency, XH\textsubscript{2} must rapidly and selectively dehydrogenate under 1 atm of H\textsubscript{2}, even though a H\textsubscript{2} atmosphere would normally be expected to inhibit dehydrogenation reactions. The dehydrogenated liquid X must also rapidly and selectively hydrogenate under 1 atm of H\textsubscript{2}. The working fluids (XH\textsubscript{2}/X) should otherwise remain chemically stable, at all operating temperatures, to avoid the necessity of separation/purification units to isolate the H\textsubscript{2} produced. As the H\textsubscript{2} would be continuously evolved and consumed within our TRFC system, XH\textsubscript{2} does not require a high hydrogen storing density to be viable: one mole of H\textsubscript{2} released per mole of XH\textsubscript{2} would be sufficient. As such, any vehicle containing our TRFC system would not require an on-board H\textsubscript{2} storage system. The dehydrogenation catalyst must be heterogeneous to prevent the catalyst from dispersing throughout the system where it could continue to catalyze the dehydrogenation reaction, thereby generating H\textsubscript{2} bubbles throughout the system, and potentially catalyzing the
hydrogenation reaction outside of the cathode, thus rendering the system inefficient. If a homogeneous dehydrogenation catalyst were to be used instead, it would likely interfere with the heterogeneous catalyst in the fuel cell, possibly inhibiting it or rendering it inactive. It is also likely that any potential homogeneous dehydrogenation catalyst would be less robust than its heterogeneous counterpart. Ideally, the catalyst would provide a very high selectivity of 99.0 to ≥ 99.9 % for X, because conversion of X to unreactive by-products would rapidly decrease the electrical current generated by the fuel cell.

It is important to note that the dehydrogenation of XH₂, and the hydrogenation of X, are the forward and reverse reactions of the same equilibrium, the position of which is temperature dependent (Figure 23). Hydrogenation is an exothermic process, and thus it is expected to be favoured at the lower temperatures of 100 °C proposed for our TRFC. In turn, the dehydrogenation of XH₂ is endothermic and should be favoured at our system’s higher temperatures of 200 °C. For our TRFC system to operate effectively, it is necessary that this temperature difference be maintained between the dehydrogenation chamber and fuel cell to ensure that the dehydrogenation/hydrogenation equilibrium compositions are sufficiently different for efficient energy conversion to take place. These requisite operating temperatures are advantageous, however; they make our TRFC system appropriate for higher temperature waste heat applications, such as in long haul trucking vehicles.

\[
\text{XH}_2 \rightleftharpoons \text{X} + \text{H}_2
\]

Favored at 200 °C    Favored at 100 °C

**Figure 23** Temperature dependent equilibrium between the hydrogenated liquid XH₂, and the dehydrogenated liquid, X.
2.1.3 Vehicular implementation

We envision our TRFC system supplementing or supplanting the alternator of a long haul trucking vehicle. An alternator is responsible for converting the mechanical energy of a vehicle’s ICE into electrical energy. It is connected to the engine via the drive belt; as the pistons of the engine move, the drive belt spins the alternator’s rotor shaft. The rotor shaft comprises poles placed around a wire coil that is wrapped around an iron core; as the rotor shaft spins, it generates a magnetic field that induces a current. This current can then be used to power the vehicle’s electrical components (i.e. lights, stereo system, etc.).\(^8\) An alternator consumes approximately 2-10\% of the total energy from fuel in a vehicle;\(^9\) even if our TRFC system could only supplement this consumption by a few percent, the fuel savings could be quite significant for the long haul trucking industry.

To ensure that our TRFC system is maintained at the appropriate operating temperatures, it will likely be placed within proximity of the vehicle’s exhaust system. A vehicle’s ICE’s cooling system, a mixture of air and liquid cooling, is very efficient at maintaining the engine at approximately 100 °C. The liquid coolant itself, often a 50:50 or 70:30 mixture of water and glycol, usually gets no hotter than 135-160 °C;\(^10\) while this would be sufficient for operating our TRFC’s fuel cell, it would not be sufficient for operating the dehydrogenation reactor. The exhaust system of diesel-powered ICES, however, can reach temperatures between 540-680 °C,\(^11,12\) and upwards of 720 °C.\(^12,13\) The catalytic converter, a component of the exhaust system responsible for reducing harmful emissions from combusting fossil fuels, can itself reach temperatures between 200-400 °C,\(^14,15\) and upwards of 850 °C.\(^16\) A vehicular exhaust system could provide more
than enough thermal energy to operate our TRFC system, and so it will likely operate within proximity to the vehicle’s exhaust.

2.2 Preliminary work on the TRFC system

2.2.1 Preliminary TRFC system development

Dr. Andrew Carrier was responsible for the preliminary development of the TRFC project, as described in his dissertation. This section highlights his contributions to the project.

Dr. Carrier was tasked with finding a suitable candidate for the working fluid of the TRFC system; one that would meet all of the criteria outlined in Section 2.1.2: rapid, selective and reversible dehydrogenation/hydrogenation under 1 atm of H₂ at 200 °C and 100 °C, respectively. Only compounds with one reactive moiety were to be considered, as a high gravimetric hydrogen capacity was deemed unnecessary. It was recognized that the dehydrogenation reaction of any candidate compound should be as endothermic as possible so that the working fluid could act efficiently as a heat sink, but not so high as to inhibit the hydrogenation reaction. Carrier determined that dehydrogenation is generally more endothermic for C–O bonds (alcohol to ketone), C–N (amine to imine), and C–C bonds (alkane to alkene), respectively; this trend can be calculated from literature bond dissociation energy values or from ΔH_f values for representative compounds. Having identified these three classes of candidate compounds, Carrier set out to test their viability
as working fluids by establishing which could react selectively and which would be susceptible to side product formation under the TRFC’s projected operating conditions.

The representative liquids chosen for initial testing from the identified classes of candidate compounds were two heteroaromatic substrates, N-methylindole and benzofuran, and a phenyl ketone, propiophenone. These compounds were hydrogenated under 1 atm of H\textsubscript{2} and compared for % conversion (i.e. rate) and selectivity (Table 3). Pd/C was chosen as the catalyst for initial screening due to its well-established use as a hydrogenation catalyst\textsuperscript{20,21} The carbon-carbon double bond of benzofuran, and the carbon-oxygen double bond of propiophenone rapidly and selectively hydrogenated under 1 atm of H\textsubscript{2} at 100 °C; the carbon-carbon double bond of N-methylindole did not, and thus it was eliminated as a viable option. Carrier speculated that a potential cause for N-methylindole’s poor reactivity may have been the nature of both the starting material and hydrogenated product, N-methylindoline. N-methylindole and N-methylindoline contain a tertiary amine functionality. Such functionalities are basic and may cause the compound to bind irreversibly to the surface of the catalyst, effectively poisoning it and causing a low conversion.
Table 3 Hydrogenation of selected unsaturated compounds under ambient pressure.$^{a,17,19}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Product</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
<td>100</td>
<td>≥99</td>
</tr>
<tr>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
<td>79</td>
<td>≥99</td>
</tr>
</tbody>
</table>

$^a$ Performed with 0.1 mol% Pd/C, 10 wt%, reduced. Mixtures were flushed with 1 atm H$_2$ and heated with stirring to 100 °C for 6 h. Conversion and selectivity were determined by $^1$H NMR spectroscopy. $^b$ Poor and non-quantifiable conversion and selectivity.

With N-methylindole eliminated as a potential working liquid, the investigation into 2,3-dihydrobenzofuran and 1-phenyl-1-propanol continued; both were dehydrogenated at 200 °C over Pd/C (Table 4). For the initial testing, the reaction mixtures were sparged with Ar in order to minimize the chance of hydrogenolysis: the catalytic cleavage of bonds (e.g. C-C, C-O, etc.) by hydrogen.$^{22a}$ 1-Phenyl-1-propanol dehydrogenation gave excellent selectivity for the desired product, propiophenone, while 2,3-dihydrobenzofuran dehydrogenation selected for both the desired product, benzofuran, and 2-ethylphenol, an undesired hydrogenolysis side product. The extent to which 2,3-dihydrobenzofuran hydrogenolysed was unexpected, given that the reaction had been sparged with Ar. Therefore, 2,3-dihydrobenzofuran was deemed an unsuitable candidate for the TRFC system.
Having eliminated both heteroaromatic substrates, N-methylindole and benzofuran, it was necessary to establish whether the high selectivity observed with 1-phenyl-1-propanol over Pd/C at 200 °C under a flow of Ar could be repeated under a H₂ atmosphere (Table 5). Unfortunately, the selectivity decreased significantly under 1 atm of H₂, and so a preliminary catalyst screening was undertaken to determine if it was possible to selectively catalyze the reaction pathway leading to the desired product, propiophenone. Pd/Al₂O₃ showed an improved selectivity, with a slightly lower conversion. Pd/SiO₂ improved selectivity to the point that the hydrogenolysis product, propylbenzene, was not observed in the ¹H NMR spectrum of the product mixture. Though the conversion over Pd/SiO₂ was lower than that over Pd/C, the selectivity was excellent. Therefore, 1-phenyl-1-propanol was identified as a candidate for the TRFC’s working fluid, and Pd/SiO₂ was identified as a possible dehydrogenation catalyst.
Carrier expanded the investigation of dehydrogenating alcohols to ketones, and examined alkyl diols as potential working fluids. Several short chain diols were subjected to dehydrogenation over Pd/SiO$_2$ (Table 6). Each alcohol moiety was expected to undergo sequential dehydrogenation, yielding two or three potential products from the symmetrical or unsymmetrical diols, respectively. The possibility of dehydronation with subsequent hydrogenations to the alkane was also anticipated at 200 °C, yielding even more possible by-products. The complicated $^1$H NMR spectra of the product mixtures made selectivity determination impossible by this method. Carrier reported, however, that it was obvious that the conversion was very low, and for the reaction mixtures where some of the products were identifiable, no doubly dehydrogenated products were detected. Diols were eliminated from consideration for the TRFC system.

---

### Table 5 Dehydrogenation reaction under hydrogen.$^{a,17,19}$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt% Pd/C</td>
<td>87</td>
<td>66</td>
</tr>
<tr>
<td>5 wt% Pd/Al$_2$O$_3$</td>
<td>81</td>
<td>85</td>
</tr>
<tr>
<td>5 wt% Pd/SiO$_2$</td>
<td>69</td>
<td>$\geq 99$</td>
</tr>
</tbody>
</table>

$^a$ Conversion and selectivity were determined by $^1$H NMR spectroscopy.
Table 6 Dehydrogenation of diols over Pd/SiO$_2$.$^{a,17,19}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Compound - 1H$_2$</td>
</tr>
<tr>
<td>HO–OH</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OH</td>
<td>1</td>
<td>100$^c$</td>
</tr>
<tr>
<td>OH</td>
<td>3</td>
<td>100$^c$</td>
</tr>
<tr>
<td>HO–OH</td>
<td>$b$</td>
<td>$b$</td>
</tr>
<tr>
<td>OH</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OH</td>
<td>$b$</td>
<td>$b$</td>
</tr>
</tbody>
</table>

$^a$ Performed with 0.1 mol% Pd/SiO$_2$, 5%, reduced, dry (Escat$^{\text{TM}}$ 1351). Mixtures were flushed with 1 atm H$_2$ at a rate of 10 mL/min and heated with stirring at 200 °C for 1 h. Conversion and selectivity were determined by $^1$H NMR spectroscopy. $^c$ Some change in the $^1$H NMR spectrum was observed but product signals could not be assigned. $^c$ No side products were observed.

Carrier also considered the dehydrogenation of amines to imines. He did recognize, however, that the use of imines as working fluids posed certain challenges: imines are susceptible to hydrolysis, particularly under acid catalyzed conditions as are prevalent in a fuel cell membrane; primary amines are known to disproportionate under reducing conditions;$^{23}$ and both amines and imines are basic enough to potentially poison a catalyst surface. Despite these challenges, however, primary and secondary benzylic amines were dehydrogenated over Pd/SiO$_2$, and the results compared to their analogous alcohols (Table 7). The majority of the amines showed little to no reactivity. α-Methyl
benzylamine did react, although it dehydrogenated into many different products. In comparison, the dehydrogenation of the analogous benzylic alcohol, 1-phenylethanol, proceeded with high conversion and selectivity. This was expected given the previous success with 1-phenyl-1-propanol over Pd/SiO₂. The dehydrogenation of benzyl alcohol, however, proceeded with an unexpectedly low conversion. Consequently, amines and primary alcohols were eliminated as potential working fluids for our TRFC system.

Carrier concluded that benzylic alcohols were the main contenders for the TRFC’s working fluid; particularly 1-phenyl-1-propanol, which has a high boiling point of 219 °C (propiophenone boiling point: 218 °C), low volatility, and demonstrated selective reactivity under the dehydrogenation reaction conditions – the most rigorous conditions of the proposed TRFC system. While Carrier did not consider the solubility of H₂ within each potential working fluid when drawing his conclusions, or consider its effect on the dehydrogenation/hydrogenation kinetics, it was not expected to be a limiting factor: in vapour-liquid systems, the H₂ fugacity of both phases is equal. Consequently, 1-phenyl-1-propanol was selected as the TRFC’s working fluid, and, thus, it became necessary to determine whether there was a sufficient difference between the equilibrium compositions at the TRFC system’s temperature extremes (100 °C and 200 °C).
Table 7 Dehydrogenation of benzylic alcohols and amines over Pd/SiO$_2$.$^{a,17,19}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Hydrogenolysis Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Product</td>
<td></td>
</tr>
<tr>
<td><img src="" alt="Chemical Structure" /></td>
<td>3</td>
<td>100$^d$</td>
<td>0</td>
</tr>
<tr>
<td><img src="" alt="Chemical Structure" /></td>
<td>$b$</td>
<td>$b$</td>
<td>$b$</td>
</tr>
<tr>
<td><img src="" alt="Chemical Structure" /></td>
<td>1</td>
<td>100$^d$</td>
<td>0</td>
</tr>
<tr>
<td><img src="" alt="Chemical Structure" /></td>
<td>49</td>
<td>100$^d$</td>
<td>0</td>
</tr>
<tr>
<td><img src="" alt="Chemical Structure" /></td>
<td>$c$</td>
<td>$c$</td>
<td>$c$</td>
</tr>
<tr>
<td><img src="" alt="Chemical Structure" /></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ Performed with 0.1 mol% Pd/SiO$_2$, 5%, reduced, dry (Escat™ 1351). Mixtures were flushed with 1 atm H$_2$ at a rate of 10 mL/min and heated with stirring at 200 ºC for 1 h. Conversion and selectivity were determined by $^1$H NMR spectroscopy. $^b$ Some change in the $^1$H NMR spectrum was observed but product signals could not be assigned. $^c$ Many different products generated, but product signals could not be assigned. $^d$ No side products were observed.
Carrier’s co-supervised undergraduate student, John Vandersleen, was tasked with measuring the equilibrium constant at particular temperatures over the desired range (100, 120, 140, 160, 180 and 200 °C), starting from both pure 1-phenyl-1-propanol (XH₂) and propiophenone (X). The reactions were carried out over 0.1-1.0 mol% loading of a 5 wt% Pd/SiO₂, under 1 atm of H₂. For the lowest temperatures investigated, Vandersleen increased the catalyst loadings to ensure equilibrium was reached in a reasonable time. The equilibrium constants for the dehydrogenation reaction were then calculated assuming only X, XH₂ and H₂ were involved in the equilibrium expression (Table 8).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>K</th>
<th>X_{XH₂} b</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.2</td>
<td>0.457</td>
</tr>
<tr>
<td>180</td>
<td>0.45</td>
<td>0.674</td>
</tr>
<tr>
<td>160</td>
<td>0.23</td>
<td>0.790</td>
</tr>
<tr>
<td>140</td>
<td>0.13</td>
<td>0.855</td>
</tr>
<tr>
<td>120</td>
<td>0.05</td>
<td>0.939</td>
</tr>
<tr>
<td>100</td>
<td>0.02</td>
<td>0.967</td>
</tr>
</tbody>
</table>

K is calculated from the mole fractions of the ketone and alcohol, and the partial H₂ pressure in the reaction vessel (1 atm). a Mole fraction of the alcohol at the equilibrium, wherein the mole fraction of H₂ is neglected.

Vandersleen determined that the equilibrium composition of the alcohol/ketone mixture is 97% 1-phenyl-1-propanol at 100 °C, and 46% 1-phenyl-1-propanol at 200 °C under 1 atm H₂ (by mole fraction, Table 8). It was expected that this would be a sufficient difference for the proposed TRFC system to function efficiently. A van’t Hoff plot of the
equilibrium data (Figure 24) indicates that the hydrogenation enthalpy and entropy of the reaction are $\Delta H^\circ = -56 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -119 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively.

![Figure 24](image-url)  

**Figure 24** van't Hoff plot for the dehydrogenation of 1-phenyl-1-propanol.\textsuperscript{19}

### 2.2.2 The project objectives

With the viability of the TRFC system established, it became necessary to optimize its two major components: the dehydrogenation and hydrogenation reactions. Dr. Darrell Dean was tasked with optimizing the hydrogenation reaction, the results of which are discussed in his dissertation.\textsuperscript{24} The optimization of the dehydrogenation reaction is described herein. The objective was to identify a heterogeneous dehydrogenation catalyst(s) that could provide a selectivity of 99.0 to $\geq 99.9\%$ for the desired product $X$, from the dehydrogenation of the working fluid $XH_2$, under the operating conditions of the reactor (i.e. 200 °C, 1 atm of $H_2$).
2.3 Experimental

2.3.1 General experimental information

Unless otherwise specified, all reagents were purchased from chemical suppliers and used as received. All organic compounds were purchased from Sigma Aldrich, Acros Organics, Alfa Aesar, and TCI America. All heterogeneous catalysts and precursors were purchased from Alfa Aesar, Pressure Chemicals and Strem. All gases were obtained from Praxair.

$^1$H NMR spectra were collected at 300 K on a Bruker AV-400 spectrometer at 400.3 MHz, and referenced relative to the deuterated solvents’ residual proton-containing solvent signal. Gas chromatography was performed using a Shimadzu GC-17A equipped with an Agilent J&W GC column with a DB-5 stationary phase (inner diameter 0.25 mm, length 30 m, film thickness 0.25 µm). Catalyst surface areas and pore size were determined using a Micromeritics Accelerated Surface Area and Porosimetry System 2010 manufactured by Micromeritics Instrument Corporation. Solution concentrations of Pd were determined on a SPECTRO ARCOS ICP-OES and Varian 820-MS Quadrupole ICP-MS instrument. Transmission electron microscopy was performed using a PHILIPS/FEI CM-20 microscope on 300/400 copper mesh and thin carbon films, and a JEOL 2011 scanning microscope. Some of the experimental methods have been described in a patent application and journal article.$^{19,25}$
2.3.2 General procedure of catalyst screening for activity and selectivity

Each reaction was performed in duplicate in the same oil bath. Into a 16 x 150 mm test tube was placed a magnetic stir bar, the appropriate catalyst at 0.1 mol% loading relative to the alcohol, and 1 mL (0.0073 mol) of 1-phenyl-propanol. The test tube was then fitted with a rubber septum. To maintain the reaction under an atmosphere of H₂, the H₂ gas was introduced to the test tubes through a 4-port gas manifold fitted with Fisherbrand tubing, a 3 mL syringe barrel (without plunger) tubing, and a hollow 12” PT2 Hamilton needle. The needle was inserted through the septum so that H₂ could flow into the test tube and the tip of the needle was positioned above the top of the liquid to facilitate maximum air displacement. A small 25 gauge, hollow needle tip was also inserted through the septum to act as a vent. Each test tube was purged with a high flow of H₂ for 15-20 min to replace the air atmosphere within the test tubes prior to exposure to heat. A bubbler was attached to the end of the gas manifold to prevent a buildup of pressure, and so that H₂ pressure could be maintained throughout the reaction’s duration. After 15 min of gas-phase purging, each test tube was lowered into an oil bath at a depth no greater than the height of liquid in the test tube and was stirred using a stir plate that was underneath the oil bath. Each tube was then maintained for 1 h at 200 °C under a low dynamic flow of H₂ with constant stirring. After the one hour, each test tube was removed from the oil bath and placed in ice to quench the reaction. Once the reaction mixture was cooled to 0 °C, the catalyst was separated from the organic liquid by filtering the mixture through a glass disposable pipette fitted with a lint-free tissue plug. Initially, a ¹H NMR spectrum of the organic liquid in chloroform-d was acquired. Side
products 1-cyclohexylpropane, 1-cyclohexyl-1-propanol, and cyclohexyl ethyl ketone were identified by comparison with $^1$H NMR spectra of the respective pure compounds, and were confirmed as potential side products in the literature.\textsuperscript{26} Side product 1-cyclohexenyl ethyl ketone was confirmed by electron ionization mass spectrometry (EI-MS) and comparison with spectra from the NIST EI-MS library. Any potential catalysts that did provide the required selectivity were analyzed for surface area and pore size.

Product mixtures exhibiting good selectivity were analyzed by GC in order to determine the % selectivity to 2 decimal places. Samples to be analyzed by GC were diluted with 15 mL HPLC grade methanol and 100 µL of hexadecane (internal standard) in a 20 mL screw cap vial. The dilute solution was mixed by inversion 15 times. From the dilute solution, 150 µL was pipette into another 15 mL HLPC grade methanol, in a 20 mL screw cap vial, and mixed by inversion 15 times. All sample constituents, and their respective amounts, were quantitatively determined via an optimized GC method with internal standardization. The method was optimized by Dr. Darrell Dean and is outlined in his dissertation (see Section 2.7: Appendix). \textsuperscript{24}

\subsection*{2.3.3 Determination of the limit of detection (LOD) for $^1$H NMR spectroscopy}

A $^1$H NMR spectrum was obtained (number of scans: 32; line broadening: 1) from a product mixture from the dehydrogenation of 1-phenyl-1-propanol with a conversion of 36 \%. The smallest peak that could be identified with confidence as being three times the intensity of the noise in the baseline was identified as a broad singlet at 5.5 ppm, and was
assumed to be representative of 2 vinyl protons. The signal’s integral value was compared with the integral values for the 1-phenyl-1-propanol benzylic proton, the propiophenone methyl protons, and the proton signals representative of the known side products. It was determined that this peak corresponded to a % composition of 0.15 and % selectivity of 0.5.

2.3.4 Determination of the limit of detection (LOD) for GC analysis

The calculations for determining % conversion and selectivity by \(^1\)H NMR spectrometry for the dehydrogenation of 1-phenyl-1-propanol with Pd/SiO\(_2\) (Section 2.3.3) were manipulated to determine what amount of side-product (i.e. propylbenzene) would be necessary to affect the second decimal place of the reaction’s selectivity (i.e. 99.995%). A standard solution of propylbenzene of the appropriate concentration (calculated to be 0.00022 M) was generated and analyzed by GC to determine whether a side-product of that relative concentration could be detected by GC analysis. The side-product peak was much greater than three times the intensity of the noise in the baseline, indicating that GC analysis can report % selectivity to 3 decimal places with confidence.

2.3.5 Determination of Pd leaching from Pd/SiO\(_2\) by ICP-MS analysis

The ICP-MS analysis of 1-phenyl-1-propanol and Catalyst Cycle 1 was performed by Evelyne Leduc, MSc, from Queen's facility for isotope research, QFIR. Ms. Leduc provided the following experimental procedure.
Samples were weighted into clean 15 mL flat-bottom PFA (Teflon) savillex vials and set to evaporate at 70 °C overnight. Approximately 10 drops of concentrated HNO₃ (1x distilled) were added to each sample and they were set to digest at 200 °C for approximately 1 h. The samples were then left to cool and evaporate overnight again at 70 °C. 1-Phenyl-1-propanol grew some unknown crystal phase during that time, and it was decided to attempt further digestion. Ten more drops of concentrated HNO₃ (1x distilled) were added to all samples and they were digested again at 180°C for approximately 1 h. The samples were then left to cool and evaporate to dryness at 70 °C. Once dry, a few millimeters of 2% HNO₃ with internal standard were added to each sample to re-dissolve them. The sample (catalyst cycle 1) was sonicated for approximately 5 min and diluted with more 2% nitric. 1-Phenyl-1-propanol had quite a bit of persistent residue and was sonicated for approximately 10 min prior to dilution with 2% nitric acid; once diluted, it was sonicated for another 10 min in an effort to dissolve as much of the residue as possible. The samples were then analyzed for Pd concentration using an Element 2 ICP-MS, with calibration standards ranging from 50 ppt to 500 ppb in concentration.

The ICP-MS analysis of catalyst cycle 6 and 15 was performed by postdoctoral fellow Dr. Alemayehu Asfaw of the Beauchemin group at Queen’s University (catalyst cycle 6/15). Dr. Asfaw provided the following procedure.

The organic liquid from a dehydrogenation of 1-phenyl-1-propanol (2 mL) over Pd/SiO₂ was isolated from the catalyst by filtration. The liquid was then mixed with aqua regia
(1:3 ml HNO₃: HCl) and heated at 60 °C for 1 h and then at 120 °C for 2 h to digest the organic constituents. The mixture was heated to dryness. Due to incomplete digestion, 10 mL of a 4 % solution of HNO₃ was added to the dried sample, and left overnight to complete leaching of palladium from the solid phase into the aqueous phase. A suspension formed, which was filtered to remove the organic particulates. The supernatant of the filtered sample was then analyzed for Pd content by ICP-MS. The calibration standards (which were prepared in 4% HNO₃) were 1-100 ppb.

### 2.3.6 Alternative working fluid studies

Each reaction was performed in duplicate, using the same oil bath. Into a 16 x 150 mm test tube was placed a magnetic stir bar, the appropriate catalyst at 0.1 mol% loading relative to the alcohol, and 1 mL of 1-(4-trifluoromethyl)phenyl-1-ethanol (0.0065 mol), 1-(4-fluorophenyl)-1-ethanol (0.008 mol), 1-(3-trifluoromethylphenyl)-1-propanol (0.0059 mol), or 1-(4-tert-butylphenyl)-1-propanol (0.005 mol). The test tube was then fitted with a 24-gauge rubber septum. To maintain the reaction under an atmosphere of H₂, the H₂ gas was introduced to the test tubes through a 4-port gas manifold fitted with tubing, a 3 mL syringe barrel (without plunger) and a 12” PT2 Hamilton needle. The needle was inserted through the septum so that H₂ could flow into the test tube and the tip of the needle was positioned just above the top of the liquid to facilitate maximum air displacement. A small 25-gauge needle tip was also inserted through the septum to act as a vent for the H₂ being introduced into the test tube, allowing any air within the volume of the test tube to be displaced. Each test tube was purged with a high flow of H₂ for 15-
20 min to replace the air atmosphere within the test tubes prior to exposure to heat. A bubbler was attached to the end of the gas manifold to prevent a buildup of pressure, and so that H₂ pressure could be maintained throughout the reaction’s duration. After 15-20 min of atmospheric purging, the small 25-gauge needle was removed and the Hamilton needle was repositioned so that the tip was at the top of the test tube, just below the end of the septum. Each test tube was then lowered into the oil bath to a depth no greater than the height of liquid in the test tube and was stirred using a stir plate that was underneath the oil bath. Each reaction was then run for 1 h at 200 °C under a low dynamic flow of H₂ (through the bubbler) with constant stirring. After the hour, each test tube was removed from the oil bath, and each test tube was placed in ice to quench the reaction. Once the reaction mixture was cooled to 0 °C, the catalyst was separated from the organic liquid by filtering the mixture through a lint-free tissue plug. The product mixture was analyzed by ¹H NMR spectroscopy and/or qualitatively assessed by GC analysis, via the GC method optimized for 1-phenyl-1-propanol.

2.3.7 Synthesis of Pd(100) nanocubes

This procedure was outlined in the literature.²⁷ Polyvinylpyrrolidone, 40 000 Mw (PVP, 106 mg, 9.5 x 10⁻⁴ mol), L-ascorbic acid (61 mg, 3.4 x 10⁻⁴ mol), KCl (185 mg, 0.0025 mol), KBr (4.7 mg, 3.9 x 10⁻⁵ mol), and Na₂PdCl₄ (57.3 mg, 1.95 x 10⁻⁴ mol) were dissolved in deionized H₂O (11 mL). The reaction mixture was transferred to a 50 mL RB fitted with a stir bar and a reflux condenser, refluxed at 80 °C for 3 h, cooled to RT and stored under Ar. The desired nanoparticles were isolated from the reaction mixture by
flocculation: 1 mL of the reaction mixture was transferred to a 1 L Teflon screw cap container, and dissolved in acetone (400 mL). The container was inverted and vented 5-6 times, and the solution left to sit for 1 week to allow the nanoparticles to flocculate. When the supernatant was clear, the acetone was decanted and the nanoparticles were suspended in 5 mL HLPC grade methanol (MeOH). The nanoparticles were then analyzed by TEM. The average nanoparticle width was determined to be 8.6 nm ± 1.8 nm.

2.3.8 Synthesis of Pd(111) nanoctahedra

This procedure was outlined in the literature.²⁷ PVP (106 mg, 9.5 x 10⁻⁴ mol), citric acid (180 mg, 9.37 x 10⁻⁴ mol) and Na₂PdCl₄ (57 mg, 1.95 x 10⁻⁴ mol) was dissolved in anhydrous EtOH (3 mL) and deionized H₂O (8 mL). The reaction mixture was transferred into a 50 mL RB fitted with a stir bar and a reflux condenser, refluxed at 80 °C for 3 h, cooled to RT, and stored under Ar. The desired nanoparticles were isolated from the reaction mixture by flocculation: 1 mL of the reaction mixture was transferred to a 1 L Teflon screw cap container and dissolved in acetone (400 mL). The container was inverted and vented 5-6 times, and the solution left to sit for 1 week to allow the nanoparticles to flocculate. When the supernatant was clear, the acetone was decanted and the nanoparticles were suspended in 6 mL of HLPC grade methanol (MeOH). The nanoparticles were then analyzed by TEM. The average nanoparticle width was determined to be 9.1 nm ± 2.2 nm.
2.3.9 Synthesis of large Pd(100) cubes

This procedure was outlined in the literature. PVP (105 mg, 9.4 x 10^{-4} mol), L-ascorbic acid (60.3 mg, 3.4 x 10^{-4} mol), and KBr (600 mg, 0.005 mol) were dissolved in deionized H₂O (8 mL) in a 20 mL screw top vial, with a stir bar. The solution was heated at 80 °C for 10 min. Na₂PdCl₄ (57.3 mg, 1.95 x 10^{-4} mol) was dissolved in deionized H₂O (3 mL) and added to the heated solution via a short-stemmed pipette. The vial was capped with a septum and vented with a hollow bore needle. The reaction mixture set stirring for 3 h at 80 °C, after which it was allowed to cool to RT with stirring overnight. The nanoparticles were washed and isolated via centrifugation. The total volume of the reaction mixture exceeded the capacity of the centrifuge tubes, and so it was divided between two centrifuge tubes to facilitate isolation. Deionized water (2 mL) was added to each centrifuge tube, and the mixture was centrifuged until the nanoparticles were separated from the solution. The supernatant was decanted, the nanoparticles were re-suspended in deionized water (2 mL), and then centrifuged. This procedure was repeated a total of 4 times. HPLC grade MeOH (1 mL) was added to each centrifuge tube to re-suspend the nanoparticles. The samples were then centrifuged to extract any residual H₂O. After decanting the MeOH (1 mL), the nanoparticles were re-suspended in HPLC MeOH or deionized H₂O and stored at 5 °C. The HPLC MeOH solution of suspended nanoparticles was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the Pd concentration (Section 2.3.10). The Pd concentration was found to be 2616 ± 14 mg/L. The nanoparticles were then analyzed by TEM. The average nanoparticle width was determined to be 19.9 nm ± 2.4 nm.
2.3.10 Determination of Pd concentration by ICP-OES for large Pd(100) cubes

The ICP-OES analysis of the large Pd(100) cubes was performed by Yoseif Makonnen of the Beauchemin group at Queen’s University. Mr. Makonnen provided the following procedure.

The research was conducted on a radial view ARCOS ICP-OES instrument (SPECTRO Analytical Instruments, Kleve, Germany) fitted with a cross-flow nebulizer and a Scott-type double-pass spray chamber. Standard solutions containing 0.1 – 1000 mg/L Pd in ultrapure 2 % (v/v) HNO₃ were prepared daily from commercially available 1000 mg/L single element standard solutions (SCP Science, Quebec, Canada) and doubly deionized water (DDW) (Arium Pro UV DI, Sartorius Stedium Biotech, Göttingen, Germany). Optimizing the nebulizer flow rate was done to arrive at a compromised set of conditions that would maximize sensitivity for Pd and the Mg²⁺ / Mg⁺ ratio. To evaluate the robustness of the plasma, the blank subtracted ratio of Mg²⁺ 280.270 nm / Mg⁺ 285.213 nm line intensities were monitored during optimization, with robust conditions being achieved at ratios ≥ 10. The standard solutions were aspirated in order of increasing concentration, followed by a rinse period of 10 minutes and the aspiration of the supplied sample. The sample was diluted by 100 fold for the purposes of sample conservation and ensuring the measured intensities would fall within the linear dynamic range of the ARCOS instrument. The intensities were blank subtracted and the Pd concentrations were determined by linear interpolation, using the external calibration standards. There were 5 replicates. No internal standardization or matrix matching methods were used in the
analysis. The analytical lines for Pd selected were 229.651 nm (ionic) and 324.270 nm (atomic).

2.3.11 General procedure for testing the activity of synthesized Pd nanoparticles

Each reaction was performed in duplicate, using the same oil bath. Into a 25 x 150 mm test tube was placed a magnetic stir bar, the appropriate amount of HPLC MeOH suspended nanoparticles to achieve 0.1 mol% Pd loading relative to the alcohol, and 1 mL (0.0073 mol) of 1-phenyl-1-propanol. The MeOH was removed under vacuum, with low heat (30-50 °C) as needed. The test tube was then fitted with a 24-gauge rubber septum. To maintain the reaction under an atmosphere of H₂, the H₂ gas was introduced to the test tubes through a 4-port gas manifold fitted with tubing, a 3 mL syringe barrel (without plunger) and a 12” PT2 Hamilton needle. The needle was inserted through the septum so that H₂ could flow into the test tube and the tip of the needle was positioned just above the top of the liquid to facilitate maximum air displacement. A small 25-gauge needle tip was also inserted through the septum to act as a vent for the H₂ being introduced into the test tube, allowing any air within the volume of the test tube to be displaced. Each test tube was purged with a high flow of H₂ for 15-20 min to replace the air atmosphere within the test tubes prior to exposure to heat. A bubbler was attached to the end of the gas manifold to prevent a buildup of pressure, and so that H₂ pressure could be maintained throughout the reaction’s duration. After 15-20 min of atmospheric purging, the small 25-gauge needle was removed and the Hamilton needle was repositioned so that the tip was at the top of the test tube, just below the end of the
septum. Each test tube was then lowered into the oil bath to a depth no greater than the height of liquid in the test tube and was stirred using a stir plate that was underneath the oil bath. Each reaction was then run for 1 h at 200 °C under a low dynamic flow of H\textsubscript{2} (through the bubbler) with constant stirring. After the hour, each test tube was removed from the oil bath, and each test tube was placed in ice to quench the reaction. Once the reaction mixture was cooled to 0 °C, the catalyst was separated from the organic liquid by filtering the mixture through an alumina and/or vulcanized carbon plug. The product mixture was quantitatively assessed by GC analysis, via the GC method optimized for 1-phenyl-1-propanol.

2.3.12 General procedure for the impregnation of Pd(100) nanocubes on solid support SBA-15

This procedure was adapted from the literature.\textsuperscript{27,29} A SBA-15 supported catalyst with 5 wt\% Pd nanoparticles was desired. A newly flocculated sample of Pd(100) nanocubes (containing 5.6 mg Pd) was suspended in anhydrous EtOH (14 mL) and HPLC grade MeOH (4 mL). The SBA-15 support (53.5 mg) was suspended in deionized H\textsubscript{2}O (10 mL) and sonicated for 1 h. The Pd(100) nanocube solution (9 mL) was added to the support suspension, and heated to 80 °C for 2 h, with stirring. The mixture was then cooled to RT and allowed to stir for 36 hours. The suspensions were then transferred to centrifuge tubes, and spun down. The supernatant was removed, and replaced with deionized H\textsubscript{2}O (2 mL). The catalyst was re-suspended in the H\textsubscript{2}O and centrifuged to remove any loose Pd nanoparticles. This was repeated a total of three times. Once washed and isolated,
catalyst was stored in a vacuum desiccator for 3 weeks, and then placed in a vacuum oven at 30 °C overnight to dry. The SBA-15 supported Pd(100) nanocube catalyst was tested for activity via the previously described method (Section 2.3.2), and analyzed by TEM.

2.3.13 Removal of PVP from SBA-15 supported Pd(100) nanocubes

This procedure was adapted from the literature.\textsuperscript{30,31} SBA-15 supported Pd(100) nanocubes (22 mg) were transferred to a crucible and heated in a muffle furnace at 280 °C for 1.5 h. The catalyst-containing crucible was cooled to RT overnight. The crucible and SBA-15 supported Pd(100) nanocubes was weighed before and after the thermal treatment; there was a mass difference of 2 mg. The thermally treated catalyst was tested for activity via the previously described method (Section 2.3.2), and analyzed by TEM.

2.3.14 Synthesis of alternative working fluid, 1-(4-tert-butylphenyl)-1-propanol

4-Tert-butylpropiophenone (1 mL, 0.005 mol) was dissolved in EtOH (10 mL). Sodium borohydride (NaBH\textsubscript{4}) (0.4 g, 0.01 mol) was added to the solution all at once with stirring. The mixture was maintained below 30 °C and stirred overnight. Cold deionized water (10 mL) was then added to the mixture, followed by the drop wise addition of a saturated ammonium chloride (NH\textsubscript{4}Cl) aqueous solution (6 mL). The desired product was extracted into ether (20 mL), which was then washed with saturated sodium chloride (NaCl)
aqueous aqueous solution, and dried with magnesium sulfate (MgSO₄). The solvent was removed under vacuum. The clear, colorless product was evaluated by 1-D (¹H) and 2-D (COSY, HSQC) NMR, as well as high-resolution electron impact mass spectrometry (HR EI-MS). Yield: Quantitative. ¹H NMR (chloroform-d): 0.94 (t, J=7.42 Hz, 3 H, H₃), 1.33 (s, 9 H, H²(CH₃)₃), 1.72 - 1.88 (m, 3 H, H²/OH), 4.58 (br dd, J=6.63 Hz, 1 H, Hⁱ), 7.28 - 7.31 (m, 2 H, H⁵/⁶'), 7.37 - 7.41 ppm (m, 2 H, H⁶/⁶'). HSQC (¹³C, chloroform-d): 9.8 (C³), 31.3 (C²(CH₃)³), 31.3 (C²), 75.8 (C¹), 125.7 (C⁵/⁶'), 125.2 ppm (C⁶/⁶'). HR EI-MS: C₁₃H₂₀O, 192.1508 m/z (measured); 192.1514 m/z (calculated). See Section 2.8: Appendix for NMR spectra.
2.4 Results and discussion

Dr. Andrew Carrier performed the preliminary development of the TRFC project (Section 2.2.1), and he concluded that benzyl alcohols, specifically 1-phenyl-1-propanol, would be effective working fluids for the TRFC system. During his investigation of 1-phenyl-1-propanol, Dr. Carrier identified Pd/SiO$_2$ as a potential dehydrogenation catalyst (Figure 25). It was necessary, however, to determine if Pd/SiO$_2$ is the best possible dehydrogenation catalyst for the TRFC system: if it is robust and resistant to leaching under the operating conditions of the TRFC system, and if it exhibits the best possible selectivity for the dehydrogenated liquid, propiophenone.

![Chemical reaction](image)

**Figure 25** Contending fluid-catalyst pair for the TRFC system.

Ideally, the selectivity of the dehydrogenation reaction would be $\geq 99.9\%$, such that the combined selectivities of the dehydrogenation and hydrogenation reactions would be 99.9\%. Such high selectivities are essential for maintaining the TRFC system’s activity over long periods of operation, before it becomes necessary to replace the working fluid (Figure 26). With a combined selectivity of 99.99\% for the dehydrogenation/hydrogenation reactions, the TRFC system could survive many thousands of cycles before it becomes necessary to replenish the working fluid. If the combined selectivity is 99\%, the working fluid’s lifetime is reduced to only a few
hundred cycles. It is important to note, however, that the amount of time it would take the fluid to complete several hundred or several thousand cycles is dependent on how the final TRFC system is engineered: the volume of working fluid used and the flow rates through the system. The spent working fluid could then be burned as fuel in other ICEs.

![Graph showing the effect of reaction selectivity on the number of cycles completed before the working fluid is converted to unreactive side-products.](image)

**Figure 26** The effect of reaction selectivity on the number of cycles completed before the working fluid is converted to unreactive side-products. One cycle represents the chemical cycle of dehydrogenating and hydrogenating one XH₂ molecule, assuming that the overall selectivity for each cycle is 99.0, 99.90, or 99.99%, respectively. Overall selectivity is the product of the dehydrogenation and hydrogenation selectivities (e.g. 0.99 x 0.999 = 0.989; overall selectivity = 98.9%).

To identify the most ideal dehydrogenation catalyst and optimize the dehydrogenation reaction, a three-pronged approach was implemented: the investigation of commercially available catalysts; the investigation of working fluid modification; and the investigation of in-house catalysts.
2.4.1 The initial investigation of commercially available catalysts

The initial approach to optimizing the TRFC’s dehydrogenation reaction began with a series of commercial catalysts (Table 9), and the working fluid 1-phenyl-1-ethanol (Figure 27). Palladium, platinum, rhodium and ruthenium catalysts were considered due to their well-established activity with respect to alcohol dehydrogenation reactions.\textsuperscript{32-34} A wide variety of supports were selected due to the established effect supports can have on catalytic activity and selectivity,\textsuperscript{35} and based on their expected robustness under the reaction conditions. 1-Phenyl-1-ethanol was used in place of 1-phenyl-1-propanol due to the latter’s lack of commercial availability at the time of the project’s commencement. It was expected that there would be no appreciable difference in reactivity between the liquids given their structural similarities, and that any conclusions drawn from a system containing 1-phenyl-1-ethanol would be applicable to a system containing 1-phenyl-1-propanol. The reaction conditions for the dehydrogenation of 1-phenyl-1-ethanol (Figure 27) mirrored Carrier’s work (Section 2.2.1) with one exception: the reactions were run under an open atmosphere instead of under H\textsubscript{2}. It was expected that any catalysts exhibiting poor selectivity for the dehydrogenated product, acetophenone, under an open atmosphere would also exhibit poor selectivity under a H\textsubscript{2} atmosphere. The catalyst loading was kept low to prevent the implementation of the TRFC system from causing any unnecessary resource depletion.
Figure 27 Dehydrogenation of 1-phenyl-1-ethanol.

Table 9 Initial investigation of commercial catalysts via the dehydrogenation of 1-phenyl-1-ethanol.$^{a,19}$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Methyl Phenyl Ketone</th>
<th>Ethylbenzene$^b$</th>
<th>Unknown Side Product$^c$</th>
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<tbody>
<tr>
<td>5% Pd/SiO$_2$</td>
<td>35</td>
<td>93</td>
<td>trace</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>5% Pd/BaSO$_4$</td>
<td>60</td>
<td>98</td>
<td>trace</td>
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<tr>
<td>5% Pd/BaCO$_3$</td>
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<td>96</td>
<td>trace</td>
<td>4</td>
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</tr>
<tr>
<td>5% Pd/CaCO$_3$</td>
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<td>87</td>
<td>9</td>
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<tr>
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<td>1</td>
<td>trace</td>
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</tr>
<tr>
<td>3% Pt/CaCO$_3$</td>
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<td>79</td>
<td>trace</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>10% Pt/Al$_2$O$_3$</td>
<td>41</td>
<td>83</td>
<td>14</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1% Pt/Al$_2$O$_3$</td>
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<td>79</td>
<td>5</td>
<td>16</td>
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<tr>
<td>10% Pt/C</td>
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<td>86</td>
<td>1</td>
<td>13</td>
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<tr>
<td>5% Pt/SiO$_2$</td>
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<td>93</td>
<td>trace</td>
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<td>0.5% Ru/Al$_2$O$_3$</td>
<td>14</td>
<td>83</td>
<td>14</td>
<td>3</td>
<td></td>
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</table>

$^a$ Performed with 0.1 mol% metal at 200 °C for 1 h under open atm. Conversion and selectivity were determined by $^1$H NMR spectroscopy. $^b$ Hydrogenolysis product. $^c$ Side products not identified, but inferred to be ring hydrogenation products such as 1-cyclohexyl-1-ethanol, and ethyl cyclohexyl ketone due to thorough analysis of 1-phenyl-1-propanol reaction mixture (vide infra).
The results for the dehydrogenation of 1-phenyl-1-ethanol over selected heterogeneous catalysts were unexpected and, at least in the case of Pd/SiO$_2$, did not agree with Carrier’s previously reported results (Section 2.2.1, Table 5). During his investigation of the dehydrogenation of 1-phenyl-1-propanol over Pd catalysts, Carrier had not encountered any side products other than the hydrogenolysis product, propylbenzene. While the presence of ethyl benzene, the hydrogenolysis product of 1-phenyl-1-ethanol, was not unexpected, the presence of an additional side-product(s) was.

Based on the $^1$H NMR splitting patterns, it was hypothesized that the additional side-product(s) was the result of ring hydrogenation. The literature shows that during the selective reduction of aromatic ketones over heterogeneous catalysts, aromatic ring hydrogenation is observed in addition to hydrogenolysis (Figure 28).$^{26}$ Face-centered cubic metals, such as palladium, are particularly active towards benzene hydrogenation, even at low temperatures and pressures.$^{36}$ The identity of these additional side-products was later confirmed as ring hydrogenated species for the dehydrogenation of 1-phenyl-1-propanol (Table 10), by comparison with $^1$H NMR spectra of the respective pure compounds (Section 2.3.2).

The lack of reproducibility between Carrier’s work, with Pd/SiO$_2$ as a benzylic alcohol dehydrogenation catalyst, and the work herein was particularly worrisome: under an open atmosphere, Pd/SiO$_2$ exhibited a 93% selectivity for acetophenone, as opposed to the $>99\%$ selectivity observed for propiophenone under a H$_2$ atmosphere. Instead, it was Pd/CaCO$_3$·Pb that exhibited the highest selectivity at 99%, though the hydrogenolysis product was still clearly observed. Two other Pd catalysts, Pd/BaSO$_4$ and Pd/BaCO$_3$,
provided respectable selectivities of $\geq 96\%$, while those exhibited by the other catalysts were universally poor. It was considered, however, that the change in reaction conditions (i.e. open versus H$_2$ atmosphere) may have contributed to the irreproducibility, and so the investigation continued with 1-phenyl-1-propanol under an H$_2$ atmosphere and a wider array of catalysts (Table 10).

Figure 28 Expected side-products of the hydrogenation of aromatic ketones over heterogeneous catalysts.$^{19}$
2.4.2 The comprehensive screening of commercially available catalysts under a H\textsubscript{2} atmosphere

Table 10 Comprehensive catalyst screening for the dehydrogenation of 1-phenyl-1-propanol.\textsuperscript{a,19}

\begin{table}
\centering
\begin{tabular}{llllll}
\hline
Catalyst & Conversion \textsuperscript{(\%)} & Propiophenone & Propyl benzene\textsuperscript{b} & Ring Hydrog.\textsuperscript{c} \\
\hline
5 wt\% Pd/SiO\textsubscript{2} & 50 & > 99 & & & 0 \\
5 wt\% Pd/CaCO\textsubscript{3} & 48 & 93 & 7 & & 0 \\
5 wt\% Pd/CaCO\textsubscript{3} with & 27 & > 99 & trace & & 0 \\
1.6 \% Pb & & & & & \\
5 wt\% Pd/BaSO\textsubscript{4} & 71 & 77 & 23 & & 0 \\
5 wt\% Pd/BaCO\textsubscript{3} & 27 & > 99 & trace & & 0 \\
5 wt\% Pd/Al\textsubscript{2}O\textsubscript{3} & 51 & 98 & 1 & & 1 \\
1 wt\% Pd/PEI·SiO\textsubscript{2} & 38 & > 99 & trace & & 0 \\
3 wt\% Pd/PEI·SiO\textsubscript{2} & 49 & 92 & 8 & & trace \\
10 wt\% Pt/Al\textsubscript{2}O\textsubscript{3} & 50 & 95 & 3 & & 2 \\
5 wt\% Pt/CaCO\textsubscript{3} & 81 & 80 & 2 & & 18 \\
5 wt\% Pt/SiO\textsubscript{2} & 12 & > 99 & trace & & 0 \\
10 wt\% Pt/C & 67 & 84 & 3 & & 13 \\
10 wt\% Pt/10 wt\% Ir mesh wire & 2 & 100\textsuperscript{d} & & & 0 \\
0.5 wt\% Rh/Al\textsubscript{2}O\textsubscript{3} & 65 & 84 & 15 & & 1 \\
5 wt\% Rh/C & 61 & 92 & 6 & & 2 \\
5 wt\% Rh/Al\textsubscript{2}O\textsubscript{3} & 75 & 86 & 13 & & 1 \\
5 wt\% Ru/Al\textsubscript{2}O\textsubscript{3} & 13 & 81 & 16 & & 3 \\
0.5 wt\% Ru/Al\textsubscript{2}O\textsubscript{3} & 15 & 84 & 16 & & 0 \\
5 wt\% Ru/C & 35 & 71 & 29 & & trace \\
\hline
\end{tabular}
\footnotesize{\textsuperscript{a} Performed with 0.1 mol\% metal at 200 °C for 1 h under 1 atm of H\textsubscript{2}, with each reaction run in duplicate and results averaged. Conversion and selectivity were determined by \textsuperscript{1}H NMR spectroscopy. PEI = Polyethylenimine. \textsuperscript{b} Hydrogenolysis product. \textsuperscript{c} Ring hydrogenation products include: 1-cyclohexylpropane; 1-cyclohexyl-1-propanol; cyclohexyl ethyl ketone; 1-cyclohexenyl ethyl ketone. \textsuperscript{d} No side products observed, possibly due to low conversion}
\end{table}
Reverting back to a H₂ atmosphere from an open atmosphere made it possible to reproduce the high selectivity previously exhibited by Pd/SiO₂. In fact, the amount of side-product exhibited by each catalyst under a H₂ atmosphere was generally less than that observed under an open atmosphere. This was not expected; it was assumed that the relative amount of side-products would be less in an open atmosphere, considering that any H₂ produced could simply diffuse away, preventing it from being incorporated into any side reactions, such as hydrogenolysis. In an effort to explain these results, differences between the catalysts’ surface under an open atmosphere versus a H₂ atmosphere were considered.

Under an open atmosphere, the concentration of O₂ would be higher than under a H₂ atmosphere, increasing the likelihood of O₂ adatoms forming on the catalyst surface. The presence of such adatoms could significantly affect catalytic activity and/or selectivity: O adatoms could block the surface sites responsible for alcohol dehydrogenation, thereby lowering the dehydrogenation rate and ketone selectivity; O adatoms could assist in catalyzing side reactions, thereby increasing their reaction rates and side-product selectivities; and, O adatoms, being highly electronegative, could alter the electronic nature of the catalyst’s surface such that surface sites responsible for catalyzing alcohol dehydrogenation are deactivated, and/or surface sites responsible for catalyzing side-product formation are activated. Consequently, the poor selectivity exhibited by Pd/SiO₂ under an open atmosphere may have been caused by O adatoms, or other surface oxidation, altering its catalytic surface, thereby affecting its activity and selectivity. The H₂ rich environment of subsequent reactions would have assured that O
adatom formation was minimized, which may have contributed to the observed increase in selectivity.

Further consideration of the results outlined in Table 10 led to all ruthenium and rhodium catalysts being eliminated as viable catalysts due to their universally poor selectivity for propiophenone. Platinum catalysts also exhibited poor selectivity for propiophenone with the exception of Pt/SiO$_2$ (selectivity > 99%), which suggested that an acidic support may be necessary to obtain the desired selectivity with platinum. The conversion with Pt/SiO$_2$ was so poor, however, that it had to be eliminated as a potential dehydrogenation catalyst. While the selectivity offered by the unsupported Pt/Ir mesh wire was high (> 99%), the conversion was so low, likely due to its low surface area, that it was also eliminated as a potential catalyst.

Palladium catalysts consistently exhibited better selectivity than the other catalysts investigated, regardless of support, with Pd/SiO$_2$, Pd/BaCO$_3$, Pd/CaCO$_3$·Pb, and Pd/PEI·SiO$_2$ (PEI = polyethyleneimine) offering the best selectivities for propiophenone (> 99%). Of these catalysts, Pd/SiO$_2$ offered the best conversion at 49.0%, followed by Pd/PEI·SiO$_2$ at 38%. Pd/BaCO$_3$ and Pd/CaCO$_3$·Pb, offer the poorest conversions, both at 27%. To explain the differences between these catalysts, it was recognized that some insight may be gained by measuring and comparing their respective surface areas (Table 11). Pd/SiO$_2$ was found to have the highest surface area, followed by Pd/PEI·SiO$_2$, then Pd/CaCO$_3$·Pb and Pd/BaCO$_3$. This trend in surface areas was identical to the observed trend in conversion, suggesting that the difference in surface area was at least partly responsible for the catalyst’s differences in activity. Consequently, due to its continuing
high performance with respect to the other contending catalysts, Pd/SiO$_2$ was confirmed as the most ideal dehydrogenation catalyst for the TRFC system.

**Table 11** Measured surfaces areas and pore sizes of contending Pd catalysts.$^{19}$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m$^2$ g$^{-1}$)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt% Pd/SiO$_2$</td>
<td>253.5</td>
<td>~15-20</td>
</tr>
<tr>
<td>1 wt% Pd/PEI·SiO$_2$</td>
<td>227.1</td>
<td>~3.5</td>
</tr>
<tr>
<td>5 wt% Pd/CaCO$_3$·Pb</td>
<td>12.7</td>
<td>N/A</td>
</tr>
<tr>
<td>5 wt% Pd/BaCO$_3$</td>
<td>4.9</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**2.4.3 TEM analysis and morphological considerations of the contending catalysts**

To better understand why Pd/SiO$_2$ was such a selective catalyst, each of the contending Pd catalysts, and a selection of eliminated catalysts (Pt/CaCO$_3$, Rh/Al$_2$O$_3$, Ru/C), were analysed by transmission electron microscopy (TEM) to determine if any particular morphology was responsible for the differences in catalytic activity (Figure 29- Figure 36). Dr. Louise Weaver of the University of New Brunswick was the technician responsible for completing the analysis and consulting on the results. Of the seven catalysts analysed, the most perplexing morphology was exhibited by Pd/SiO$_2$ itself. As illustrated in Figure 29-A and Figure 29-C, Pd/SiO$_2$ largely consisted of Pd finely dispersed throughout the SiO$_2$ support as expected; however, as illustrated in Figure 29-B and Figure 29-D, Pd/SiO$_2$ was also comprised of large Pd clusters that appeared to be unassociated with the SiO$_2$ support. Dr. Weaver reported that she had never encountered such morphology before and could offer no insight as to its importance or catalytic
activity. Consequently, the expertise of Dr. Bruce Gates was sought: Gates is a specialist in heterogeneous catalysis at the University of California, Davis.\textsuperscript{37}

Figure 29 TEM images of Pd/SiO\textsubscript{2} (average particle size could not be accurately measured due to the nature of the particles).
At Dr. Gates’ request, his graduate student, Ceren Aydin, reviewed the TEM images (Figure 29). Aydin confirmed that her group was also unfamiliar with the observed morphology of Pd clusters. She did advise that the high metal loading of 5%, coupled with palladium’s penchant for sintering and/or agglomerating, may have contributed to the formation of such large Pd clusters. Aydin also suggested that the clusters may not be completely dissociated from the support: that the large clusters were simply blocking the support from view. Palladium’s penchant for agglomeration likely explains why no discrete Pd particles were observed, only Pd clusters or extended Pd networks, even when associated with the SiO₂ support.

After conferring with both Dr. Weaver and Dr. Gates, it was considered that the clusters maybe be Pd sponge, or share the morphology thereof. Sponges are highly porous metal structures that can be synthesized by a number of methods, including the thermal reduction of metal ion-impregnated porous supports, or by colloidal methods using polymer-based templates.³⁸ To test this theory, Pd sponge was purchased and analyzed by scanning electron microscopy (SEM) (Figure 30). It was recognized that the Pd sponge morphology was strikingly similar to that of the clusters comprising Pd/SiO₂ (Figure 29-B); thus, it was considered that the large Pd clusters were likely a form of Pd sponge, a potential consequence of the commercial provider’s synthetic method. Of the other Pd catalysts analysed, each exhibited some evidence of Pd sponge morphology (Pd/CaCO₃·Pb: Figure 32-A, Pd/BaCO₃: Figure 33-A), with the exception of Pd/PEI·SiO₂ (Figure 31), though none to the same extent as Pd/SiO₂.
Figure 30 SEM images of Pd sponge.
Figure 31 TEM images of Pd/PEI·SiO₂ (average particle size: 16 nm).
**Figure 32** TEM images of Pd/CaCO$_3$·Pb (average cluster size: 10.5 nm).
Figure 33 TEM images of Pd/BaCO$_3$ (average particle size: 12 nm).
The Pd particle size for each catalyst was measured and found to be relatively large: 10.5 nm (Pd/CaCO$_3$·Pb), 12 nm (Pd/BaCO$_3$) and 16 nm (Pd/PEI·SiO$_2$). The Pd particle size of Pd/SiO$_2$, however, could not be accurately measured due to the particles’ agglomerated nature; no discrete Pd particles were discernible. Pd/CaCO$_3$·Pb was similar in that only the size of discrete clusters could be measured, not particles. The Pd particles of Pd/PEI·SiO$_2$ were particularly unique, not only for their size (16 nm) and lack of Pd sponge morphology, but for the apparent cubic structure of certain particles (Figure 31-C/D). For the particles of a face-centred cubic metal like Pd to obtain a cubic structure, the particles would have to adopt six (100) faces (Section 1.7.2). (100) faces are often considered to be less thermodynamically stable than (111) faces because they possess a lower surface atom density and coordination number, leading to a higher surface energy and penchant for surface reconstructions.$^{39}$ It is typically expected for spherical particles, containing large (111) and small (100) faces, to dominate due to their minimized surface energy and area. As such, it was unexpected to observe cubic structured particles comprising Pd/PEI·SiO$_2$.

The TEM analysis of the eliminated catalysts Pt/CaCO$_3$ (Figure 34), Rh/Al$_2$O$_3$ (Figure 35) and Ru/C (Figure 36) revealed that each metal was very finely and thoroughly dispersed over its respective support. There was no evidence of sponge morphology in any of the eliminated catalysts, and their particle size was comparatively small relative to the Pd catalysts: 2-8.5 nm (Pt/CaCO$_3$), 3 nm (Rh/Al$_2$O$_3$), and ≤2 nm (Ru/C). Pt/CaCO$_3$ did show some evidence of particle agglomeration with Pt clusters approximately 8.5 nm in size, in addition to small discrete Pt particles at 2 nm. It was
recognized that particle size was likely the main contributor to the difference in selectivity between the contending Pd catalysts (Table 11), and the eliminated Pt, Rh and Ru catalysts (Table 10) for the dehydrogenation of 1-phenyl-1-propanol. The Pd catalysts were composed of large particles or particle clusters ≥ 10 nm in size; the eliminated catalysts were composed of particles ~2-3 nm in size. Generally, as particle size decreases, the total surface area available to do heterogeneous catalysis increases. As surface area increases, there is a corresponding increase in the variety of surface types and/or defects available, each of which may catalyze different reaction pathways. Therefore, in retrospect, it is no surprise that the eliminated Pt, Rh, and Ru catalysts exhibited poor selectivity for the dehydrogenation of 1-phenyl-1-propanol: their large catalytic surface area likely contained the requisite surfaces to not only catalyze 1-phenyl-1-propanol dehydrogenation, but to catalyze side-product formation as well (Figure 28). For the Pd catalysts to have achieved such high selectivities, the opposite would have to be true.

This more comprehensive screening of the most readily available commercial catalysts concluded with Pd/SiO\textsubscript{2} remaining as the dehydrogenation catalyst of choice for the TRFC system, based on selectivity and conversion as determined by NMR spectroscopy (Table 10). The catalyst screening also identified other Pd catalysts, Pd/PEI·SiO\textsubscript{2}, Pd/CaCO\textsubscript{3} and Pd/BaCO\textsubscript{3}, that could be considered for use in the TRFC system if Pd/SiO\textsubscript{2} did not stand up to more rigorous testing. Having selected Pd/SiO\textsubscript{2} as the dehydrogenation catalyst, however, it was necessary to determine if it would remain catalytically active and resistant to leaching over repeated dehydrogenation cycles.
Figure 34 TEM images of Pt/CaCO$_3$ (average particle size: 2 nm /8.5 nm).
Figure 35 TEM images of Rh/Al₂O₃ (average particle size: 3 nm).
Figure 36 TEM images of Ru/C (average particle size: ≤ 2 nm).
2.4.4 Determination of the robustness of Pd/SiO\(_2\) as a dehydrogenation catalyst

The proposed TRFC system, once implemented for industrial use, will be subjected to a spectrum of non-ideal conditions, including improper system use and storage. It was of interest, therefore, to determine whether Pd/SiO\(_2\) could maintain its high catalytic activity after being subjected to non-ideal conditions. Consequently, the same 0.1 mol\% loading of Pd/SiO\(_2\) was used for seventeen sequential dehydrogenation reactions over the course of two months (Table 12). In between reactions, the reacted fluid was left sitting over the catalyst at ambient conditions, and was siphoned off only before another dehydrogenation was completed. The catalyst was not dried between runs with the exception of cycle 17: the Pd/SiO\(_2\) was dried before use on that occasion to determine if the observed side-products were accumulating from residual working fluid. The time between reactions spanned hours, days and weeks. These conditions were meant to emulate a TRFC-fitted vehicle being driven and parked, repeatedly, over the course of two months in the summer.

Remarkably, the catalytic activity of Pd/SiO\(_2\) remained high with good selectivity for propiophenone until cycle 16 (97\% selectivity), where the catalyst’s selectivity for propylbenzene increased. The increased selectivity for propylbenzene may have been attributed to surface reduction, oxidation, or restructuring. As the reaction mixture was only siphoned off between reactions, however, it was also recognized that the decrease in selectivity could have resulted from accumulated side products from residual fluid. Subsequently, the catalyst was dried and re-tested. The selectivity did improve slightly: 98\% selectivity, up from 97\%). Had more rigorous pre-treatment methods been
implemented, it is possible the catalyst’s initial selectivity could have been restored. With no loss of catalytic activity and no significant drop in selectivity until the later reactions, the catalyst cycling results suggested that Pd/SiO$_2$ would not only survive real-world conditions in a TRFC system, it would perform well in them.

Table 12  Repeat dehydrogenations of 1-phenyl-1-propanol over the same 0.1 mol% loading of Pd/SiO$_2$.\(^a\)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Propiophenone</td>
</tr>
<tr>
<td>1</td>
<td>47</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>41</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>49</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>43</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>48</td>
<td>99</td>
</tr>
<tr>
<td>6(^e)</td>
<td>48</td>
<td>99</td>
</tr>
<tr>
<td>7</td>
<td>45</td>
<td>99</td>
</tr>
<tr>
<td>8</td>
<td>41</td>
<td>99</td>
</tr>
<tr>
<td>9</td>
<td>44</td>
<td>99</td>
</tr>
<tr>
<td>10</td>
<td>55</td>
<td>99</td>
</tr>
<tr>
<td>11</td>
<td>59</td>
<td>99</td>
</tr>
<tr>
<td>12</td>
<td>57</td>
<td>99</td>
</tr>
<tr>
<td>13</td>
<td>54</td>
<td>98</td>
</tr>
<tr>
<td>14</td>
<td>57</td>
<td>99</td>
</tr>
<tr>
<td>15</td>
<td>56</td>
<td>99</td>
</tr>
<tr>
<td>16(^e)</td>
<td>59</td>
<td>97</td>
</tr>
<tr>
<td>17(^f)</td>
<td>54</td>
<td>98</td>
</tr>
</tbody>
</table>

\(^a\) Performed with 0.1 mol% metal at 200 °C for 1 h under 1 atm of H$_2$. Conversion and selectivity were determined by $^1$H NMR spectroscopy. \(^b\) Hydrogenolysis product. \(^c\) Ring hydrogenation products include: 1-cyclohexylpropane; 1-cyclohexyl-1-propanol; cyclohexyl ethyl ketone; 1-cyclohexenyl ethyl ketone. \(^d\) Trace $= < 1\%$. \(^e\) Liquid sat over catalyst for 2-3 weeks. \(^f\) Catalyst was dried in vacuum desiccator before use.
It was noted, however, that the selectivity of the initial cycle was slightly less than what was previously observed (Table 10, Table 12): 99% selectivity with 1% side-product versus > 99% with only trace amounts of side-product. Such a small decrease in selectivity may not seem significant; however, those decreases in selectivity can appreciably decrease the working fluid’s lifetime in the TRFC system (Figure 26). It is important to note, however, that the observed decrease in selectivity does not negate the results of the catalyst cycling: it can still be concluded that Pd/SiO$_2$ would perform well under less than ideal conditions. Two possibilities for this decreased selectivity were considered: the heterogeneity of the commercial catalyst, and the environmental conditions within the catalyst was stored and used.

Following a discussion with Dr. Natalia Semagina, a heterogeneous catalysis expert at the University of Alberta, it was recognized that the difference in selectivity between the initial dehydrogenation of 1-phenyl-1-propanol over Pd/SiO$_2$ (> 99%, Table 10) and the catalyst recycling (99%, Table 12) may be attributed to the heterogeneity existent within each lot of catalyst. Variation in catalytic activity and selectivity can be expected across separate lots of heterogeneous catalysts; however variation in catalytic activity and selectivity can also be observed within the same lot of catalyst, especially if only small quantities of that catalyst are being used. During the comprehensive catalyst screening (Table 10), however, every reaction was run in duplicate to account for such sample heterogeneities and none were observed. So while it is possible that the decrease in selectivity observed for cycle 1 of the catalyst cycling was the result of sample heterogeneity, it seems unlikely. Even so, Dr. Semagina explained that any adverse
effects from sample heterogeneity may be minimized in the TRFC system once larger amounts of catalyst are being used.

The other possibility for said decrease in selectivity was humidity. During his investigation of the TRFC’s temperature dependent equilibrium with 1-phenyl-1-propanol over Pd/SiO₂ (Section 2.2.1), undergraduate student John Vandersleen reported a drop in selectivity throughout the summer months. It was considered that the atmosphere’s humidity may have adversely affected the catalyst, altering its catalytic surface, thereby increasing the rate at which side-products were formed. There is precedence in the literature for the adsorption of water onto Pd surfaces, specifically via adsorbed oxygen atoms. As described by Yoshizawa et al., adsorbed oxygen atoms result from exposing Pd catalysts to air at ambient temperatures; said adsorbed oxygen atoms then aid in the adsorption and dissociation of water on the catalyst’s surface. Through density functional theory (DFT) calculations, Yoshizawa et al. determined that adsorbed oxygen can play an important mechanistic role in reactions (i.e. the hydration of nitriles). Since Vandersleen’s investigation, and the work described herein, was carried out during the summer months, it was postulated that the decrease in selectivity could have resulted from surface-adsorbed water decreasing the rate of product formation, or increasing the rate of side-product formation. Vandersleen found that drying his catalyst under vacuum at 150 °C for three days helped improve selectivity.

To test the theory that atmospheric humidity levels were affecting the performance of Pd/SiO₂ during the dehydrogenation of 1-phenyl-1-propanol, the catalyst was pre-treated at 150 °C under vacuum for 3 days before use. The dehydrogenation of 1-
phenyl-1-propanol was performed, in quadruplicate, over the pre-treated Pd/SiO$_2$ under an H$_2$ atmosphere (Table 13). The catalyst exhibited a selectivity of >99% for propiophenone, with no trace of side-product formation, as determined by $^1$H NMR spectroscopy. This result suggests that surface adsorbed water may have been responsible for the decrease in selectivity observed during the catalyst cycling.

**Table 13** Dehydrogenation of 1-phenyl-1-propanol over pre-treated Pd/SiO$_2$.\(^{a,19}\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Propiophenone</th>
<th>Propyl benzene(^b)</th>
<th>Ring Hydrog.(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39</td>
<td>99</td>
<td>ND(^d)</td>
<td>ND</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Performed with 0.1 mol% metal at 200 °C for 1 h under 1 atm of H$_2$ with the reaction run four times. Catalyst was pre-treated at 150 °C under vacuum for 3 d. Conversion and selectivity were determined by $^1$H NMR spectroscopy. \(^{b}\) Hydrogenolysis product. \(^{c}\) Ring hydrogenation products include: 1-cyclohexylpropane; 1-cyclohexyl-1-propanol; cyclohexyl ethyl ketone; 1-cyclohexenyl ethyl ketone. \(^{d}\) ND = not detected in NMR spectra

To determine what effect repeated exposure to the TRFC’s operating conditions would have on the catalyst’s morphology, the Pd/SiO$_2$ used during the catalyst cycling was sent for TEM analysis (Figure 37). To determine the catalyst’s resistance to Pd leaching after said repeated exposure, reaction mixtures from the catalyst cycling were sent for ICP-MS analysis (Table 14).
Table 14 ICP-MS analysis of select 1-phenyl-1-propanol dehydrogenation reactions to determine extend of Pd leaching.

![Chemical Reaction Diagram]

<table>
<thead>
<tr>
<th>Cycle</th>
<th>[Pd]_{ppb}</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>8</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>47</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>48</td>
<td>99</td>
</tr>
<tr>
<td>9</td>
<td>14</td>
<td>44</td>
<td>99</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>56</td>
<td>99</td>
</tr>
<tr>
<td>17</td>
<td>10</td>
<td>54</td>
<td>98</td>
</tr>
</tbody>
</table>

*Performed with 2 mL unadulterated 1-phenyl-1-propanol. Results measured by Queen’s Facility for Isotope Research. Results were measured by Dr. Beauchemin’s ICP-MS lab at Queen’s University where Pd could not be detected in 1-phenyl-1-propanol. For complete details, see Section 2.3.5.*

Of the samples analyzed for Pd leaching, their Pd concentrations were never more than 6 ppb above the background concentration (8 ppb). There were concerns that the Pd sponge morphology observed for Pd/SiO$_2$ could result in significant Pd leaching (Figure 29). Thankfully, the anticipated high Pd leaching was not observed, which suggests that Pd/SiO$_2$ will remain a high performing, robust catalyst while under the conditions of the TRFC system.
Figure 37 TEM analysis of Pd/SiO$_2$ after catalyst cycling (average particle size: 18.5 nm).
It was noted, however, that the Pd/SiO$_2$ used for catalyst cycling showed dramatically different morphologies than previously observed for the unused catalyst (Figure 29). The Pd particles had formed into large agglomerates on the surface of the support, some upwards of 140 nm across (Figure 37-C), as opposed to the finely dispersed Pd clusters/networks previously observed. There was also no evidence of the Pd sponge morphology that had previously dominated the catalyst’s landscape. It had been considered that the sponge morphology was a potentially important contributor to the catalyst’s activity and selectivity; however, as Pd/SiO$_2$ had retained its high activity and selectivity over 17 sequential dehydrogenations, this analysis would suggest that the Pd sponge morphology is not essential to the catalyst’s performance.

To further test this theory, Pd sponge was purchased and used, as received, as the catalyst for a 1-phenyl-1-propanol dehydrogenation at 0.1 mol% loading: there was negligible conversion after 1 hour at 200 °C. The Pd sponge, however, was visibly coarser than the sponge morphology observed for Pd/SiO$_2$; as such, it could have lacked the surface area necessary for significant catalytic activity (compare Figure 29 and Figure 30). It was recognized that the Pd clusters exhibiting sponge morphology likely agglomerated onto the surface of the support, contributing to the 140 nm Pd clumps that were observed. Once a complete TRFC system has been engineered and is operational, long term studies should be undertaken to determine how much more Pd agglomeration can be expected, and what effect that will have on the catalyst’s performance.

Pd/SiO$_2$ was selected as the TRFC’s dehydrogenation catalyst by virtue of its general robustness in the face of the system’s operating conditions, and its high
selectivity for the dehydrogenation of 1-phenyl-1-propanol, as determined by NMR spectroscopy. It was necessary to determine, however, if the selectivity exhibited by Pd/SiO$_2$ was actually just slightly higher than 99%, as the NMR analysis suggested, or if it was exhibiting selectivities in excess of 99.9%. As previously discussed, the lifetime of the TRFC’s working fluid is dependent on the combined selectivities of the system’s dehydrogenation and hydrogenation reactions. A difference in selectivity of just 0.9% (99 to 99.9%) can increase the TRFC’s operational lifetime between fluid changes by several hundred cycles (Figure 26).

2.4.5 Gas chromatographic determination of the propiophenone selectivity of Pd/SiO$_2$

Gas chromatography (GC) was the analysis method of choice for determining the absolute selectivity of Pd/SiO$_2$ for the dehydrogenation of 1-phenyl-1-propanol. It was established that gas chromatography is a sufficiently sensitive enough technique to confidently report the catalyst’s selectivity for propiophenone to a minimum of 2 decimal places (Section 2.3.4). The reaction mixtures of 1-phenyl-1-propanol dehydrogenation over pre-treated Pd/SiO$_2$ (Section 2.4.3, Table 13) were the first reaction mixtures analyzed by GC (Table 15), the methodology for which was previously described.$^{24}$ Of the dehydrogenation reactions conducted in quadruplicate, the average of the two best results gave a selectivity of 99.65% for propiophenone. While this selectivity was not as high as the ideal of $\geq 99.9\%$, it was recognized that, for heterogeneous catalysis, a selectivity of 99.65% is exceptionally high. It was interesting to note, however, that
despite the exceptionally high selectivity, and no evidence of side-product formation in the NMR spectra, the GC trace distinctly showed three separate side-products: propylbenzene, 1-cyclohexyl-1-propanol, and ethyl cyclohexyl ketone (Figure 38).

**Table 15** Pd/SiO$_2$ selectivity determination by GC analysis.$^{a,19}$

<table>
<thead>
<tr>
<th>Analysis Method</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H NMR</td>
<td>39$^b$</td>
<td>$&gt;99^b$</td>
</tr>
<tr>
<td>GC</td>
<td>35 ± 2$^c$</td>
<td>99.65 ± 0.02$^c$</td>
</tr>
</tbody>
</table>

$a$ Dehydrogenation of 1-phenyl-1-propanol performed with 0.1 mol % Pd/SiO$_2$ under a 1 atm H$_2$ for 1 h at 200 °C, in quadruplicate. Catalyst was pre-treated (3 days under vacuum at 150 °C) to remove moisture.

$b$ Averaged from two separate reactions analysed in duplicate.

$c$ Averaged from two separated reactions analysed in triplicate by GC.

**Figure 38** Observed side-products of the dehydrogenation of 1-phenyl-1-propanol: propylbenzene, 1-cyclohexyl-1-propanol, and ethyl cyclohexyl ketone, respectively.

Of these observed side-products, propylbenzene was recognized as a thermodynamic sink; however, it was considered possible for 1-cyclohexyl-1-propanol and ethyl cyclohexyl ketone to dehydrogenate back into 1-phenyl-1-propanol and propiophenone under the TRFC’s dehydrogenation conditions. If it was possible to re-
aromatize the ring hydrogenation products, then concerns over Pd/SiO$_2$’s selectivity (99.65%) would be unfounded: any ring hydrogenation side-products produced would eventually convert back into functional working fluid. To test this, 1-cyclohexyl-1-propanol and ethyl cyclohexyl ketone were reacted over Pd/SiO$_2$ at 200 °C under a H$_2$ atmosphere (Figure 39). Unfortunately, no re-aromatization occurred.

![Reaction Scheme](image)

**Figure 39** Attempted ring dehydrogenation of observed side-products.

Having established that all ring hydrogenation side-products would only persist and accumulate in the TRFC system, it was recognized that shutting down the pathways leading to those side-products could increase selectivity to $\geq 99.9\%$. It was considered that, if the working fluid’s aromatic ring could be rendered electron deficient, it may prevent the ring from adsorbing to the catalyst’s surface, effectively shutting down the formation of ring hydrogenation side-products.

### 2.4.6 Investigation of ring-substituted working fluids for side-product prevention

Pd/SiO$_2$ was selected as the dehydrogenation catalyst for the proposed TRFC system. It was selected on the basis of its excellent selectivity for propiophenone
(99.65%) and robustness to the TRFC’s operating conditions (only ppb Pd leaching). However, the persistence of ring hydrogenation side-products (Figure 38) was preventing selectivities $\geq 99.9\%$ from being attained. It was considered that, if the aromatic ring of 1-phenyl-1-propanol was rendered electron deficient, it would inhibit the ring’s adsorption on the catalyst’s surface, thereby preventing ring hydrogenation. As such, three substituted benzyl alcohols were selected for investigation as alternative working fluids: 1-(4-fluorophenyl)-1-ethanol, 1-(4-trifluoromethylphenyl)-1-ethanol, and 1-(3-trifluoromethylphenyl)-1-propanol (Figure 40). These alcohols were selected specifically for their substituents’ expected stability under the TRFC’s operating conditions. The p-F and p-CF$_3$ substituents were selected to gauge the difference between having the electronegative atom (F) bonded directly to the ring, or having said atom part of a more complex substituent (p-CF$_3$); p-CF$_3$ and m-CF$_3$ were selected to determine the effect of changing the substituent’s position around the ring. The results are listed in Table 16.

![Chemical structure](image)

$X = F, CF_3$

**Figure 40** Alternative working fluids investigated to prevent side-product formation.
### Table 16 Dehydrogenation of alternative working fluids for inhibition of ring hydrogenation side-products.

![Dehydrogenation Reaction]

<table>
<thead>
<tr>
<th>X, R</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-F, Me</td>
<td>NR&lt;sup&gt;b&lt;/sup&gt;</td>
<td>---</td>
</tr>
<tr>
<td>p-CF&lt;sub&gt;3&lt;/sub&gt;, Me</td>
<td>5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>100%</td>
</tr>
<tr>
<td>m-CF&lt;sub&gt;3&lt;/sub&gt;, Et</td>
<td>trace&lt;sup&gt;b&lt;/sup&gt;</td>
<td>100%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Dehydrogenations performed with 0.1 mol % Pd/SiO<sub>2</sub> under a 1 atm H<sub>2</sub> for 1 h at 200 °C, in duplicate.

<sup>b</sup> Analysed by GC.

<sup>c</sup> Analysed by NMR.

Dehydrogenation of the substituted working fluids resulted in negligible conversions under the TRFC’s conditions. Rendering the aromatic ring electron deficient not only inhibited side-product formation, it also inhibited product formation. The currently accepted mechanism for the dehydrogenation of benzyl alcohol over Pd surfaces involves two steps:

\[
\begin{align*}
\text{Ph-CH}_2\text{-OH(ads)} & \rightarrow \text{Ph-CH}_2\text{-O(ads)} + \text{H(ads)} \\
\text{Ph-CH}_2\text{-O(ads)} & \rightarrow \text{Ph-CH=O(ads)} + \text{H(ads)}
\end{align*}
\]

**Equation 18** Mechanism of the dehydrogenation of benzyl alcohol

For there to be negligible conversion to the desired ketone for each of the alternative fluids tested, either the electron-withdrawing substituents rendered the alcohol functionality too electron deficient to adsorb to the catalyst’s surface, the adsorption of the aromatic ring is a more integral part of the dehydrogenation mechanism than was
previously recognized, or the fluorine-based substituents irreversibly bound to the catalyst’s surface. There is precedence in the literature for chloride and bromide ions irreversibly binding to Pd surfaces,\textsuperscript{27,28} so it is possible that the poor conversion is a consequence of the working fluid irreversibly binding to the catalyst’s surface. The fact that 1-(4-trifluoromethylphenyl)-1-ethanol exhibited the highest conversion of the three fluids may suggest that substituent size, which would affect adsorption of the aromatic ring, and inductive strength, which would affect adsorption of the aromatic ring and/or the alcohol functionality, are the most important factors in determining the fluid’s reactivity. The actual conversion, however, is just too low to draw any conclusions with confidence. Subsequently, these substituted benzylic alcohols had to be eliminated as a potential solution to the ring hydrogenation side-products.

Given that the electron-withdrawing nature of the working fluids’ substituents may have rendered the alcohol functionality too electron deficient to react, another alternative working fluid was considered: 1-(4-tert-butylphenyl)-1-propanol. It was anticipated that the bulk of the tert-butyl substituent would physically prevent the ring from interacting with the catalyst’s surface, thereby preventing the formation of ring hydrogenation side-products. This alternative fluid was reacted over Pd/SiO\textsubscript{2} at 200 °C under a H\textsubscript{2} atmosphere; after 1 hour, the conversion was negligible (Table 17). Given the sheer bulk of the substituent, and the generally accepted mechanism of benzyl alcohol dehydrogenation, the benzylic carbon may not have been able to interact with the catalyst’s surface in order to react.
Table 17 Dehydrogenation of alternative fluid 1-(4-tert-butylphenyl)-1-propanol for inhibition of ring hydrogenation side-products.\\(^a\)

\[
\begin{array}{ccc}
\text{X, R} & \text{Conversion} & \text{Selectivity} \\
\hline
\text{p-}^{\text{t}}\text{Bu, Et} & \text{trace}^{b} & 100 \%
\end{array}
\]

\(^a\) Dehydrogenations performed with 0.1 mol % Pd/SiO\(_2\) under a 1 atm H\(_2\) for 1 h at 200 \(^\circ\)C
\(^b\) Analysed by GC.

Unfortunately, the investigation into alternative working fluids to inhibit the formation of ring hydrogenation side-products, thereby increasing the system’s selectivity, proved unsuccessful. Consequently, an entirely different approach was sought: one that could eliminate some of the inherent heterogeneity of heterogeneous catalysts, provide insight on which surfaces were catalyzing which reaction pathways, and perhaps finally increase propiophenone selectivity to the desired \(\geq 99.9\%\): surface specific Pd nanoparticles.

2.4.7 Development of in-house surface specific Pd nanoparticles

The synthesis of size and surface specific metal nanoparticles is a very active field of research that has been well reviewed.\(^{42,43}\) Being able to control the surface structure of metal particles, to select for one face over another (e.g. 100 face versus 111 face, Section 1.7.2), allows researchers to better understand which metal surfaces are
responsible for catalyzing the desired, or undesired, pathways of their reactions. Typically, the synthesis of size and surface specific nanoparticles requires the reduction of metal precursors (e.g. H$_2$PdCl$_4$ or Na$_2$PdCl$_4$) by alcohols in the presence of a stabilizer, or capping agent, to control particle size and face selection (Equation 19).

\[
\text{H}_2\text{PdCl}_4 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{Pd}^0 + \text{CH}_3\text{CHO} + 4 \text{HCl}
\]

**Equation 19** Alcohol-reduction of metal precursors for nanoparticle synthesis.

Poly(N-vinyl-2-pyrrolidone) (PVP) is a standard stabilizer responsible for controlling particle size and stability (Figure 41). PVP interacts with metal surfaces primarily via its carbonyl functionality and protects metal nanoparticles from oxidation and/or agglomeration. PVP is often used to control particle size by varying its concentration: the higher the PVP concentration, the better the stabilization, the smaller the particles.\textsuperscript{42,44} Halide ions such as Br\textsuperscript{-} and Cl\textsuperscript{-}, and carboxylic acids such as citric acid, are often used as capping agents to select for particular faces: halide ions selectively adsorb to (100) faces,\textsuperscript{28} and citric acid will selectively adsorb to (111) faces.\textsuperscript{45} There are published and proprietary methods for removing such stabilizers and capping agents from the desired nanoparticles,\textsuperscript{27,31} however the nanoparticles are often used as synthesized.\textsuperscript{42,46} There is also precedence for washing or flocculating nanoparticles to removed excess capping agents, stabilizers and solvent before use.\textsuperscript{28,44}
While the successful synthesis of size and surface specific nanoparticles is not a trivial undertaking, it was considered a means of investigating which Pd surfaces are responsible for catalyzing the desired and undesired pathways of 1-phenyl-1-propanol dehydrogenation. For Pd catalyzed dehydrogenations of benzyl alcohol or secondary alcohols, such as isopropanol, the literature suggests that most decomposition pathways occur on Pd (111) faces, while the dehydrogenation itself can occur on both Pd(111) and Pd(100) faces. While studying the contending catalyst Pd/PEI·SiO$_2$ (Section 2.4.3), it was recognized that its high selectivity for propiophenone (> 99%) may well have been attributed to its particles’ cubic structure. To determine if Pd face specificity exists for 1-phenyl-1-propanol dehydrogenations, the synthesis of Pd (100) nanocubes and Pd (111) octahedral was proposed. The expectation was, with insight on said face specificity, the commercial Pd/SiO$_2$ catalyst could be selectively poisoned, or in-house heterogeneous catalysts could be intelligently designed, so that the desired selectivity of $\geq 99.9\%$ for propiophenone could be achieved.

In 2011, Xia et al.$^{27}$ described the synthesis of Pd (100) nanocubes and Pd (111) nanoctahedra: their outlined procedures were repeated, the synthesized nanoparticles isolated and purified by flocculation, and analyzed by TEM (Figure 42 - Figure 45).
Figure 42 Synthesis and TEM image of Pd (100) nanocubes.

Figure 43 Synthesis and TEM image of Pd(111) nanoctahedra.
Figure 44 TEM images of Pd(100) nanocubes (average particle size: 8.6 ± 1.8nm).
Figure 45 TEM images of Pd nanoparticles which include Pd(111) nanoctahedra (average particle size: 9.1 ± 2.2 nm).
The TEM analysis of the in-house synthesized Pd(100) nanocubes and Pd(111) nanocahedra revealed that, while the expected structural morphology was observed for some nanoparticles (Figure 44-A/B; Figure 45-D), there was significant morphological heterogeneity observed for others (Figure 44-C/D; Figure 45-B/C): both catalysts contained large Pd tetrahedrons, small Pd spheres, and in the case of the Pd(100) nanocubes, Pd nanobars. Both catalysts also exhibited large, amorphous Pd agglomerates. The nanobars were expected: Xia et al. reported the nanobars as a side-product of their Pd(100) nanocube synthesis. The bars were expected to possess the same (100) face as the Pd nanocubes. The tetrahedrons were likely the result of a slow Pd reduction in the presence of a high PVP concentration, as described in the literature; tetrahedrons only possess the (111) face. The average particle size of the in-house synthesized Pd nanoparticles (~ 9 nm) was larger than the average reported by Xia et al. (~ 6 nm). A large particle size was desired, however. As previous discussed in Section 2.4.3, the contending Pd catalysts for the dehydrogenation of 1-phenyl-1-propanol all possessed particles 10-16 nm in size, as compared to the eliminated Pt, Rh, and Ru catalysts with an average particle size of ~2-3 nm; this suggested that a large particle size was essential for high selectivities to be attained. Subsequently, while the Pd(100) nanocubes and Pd(111) nanocahedra did not exhibit an exceptionally high shape selectivity, it was decided to test their activity as 1-phenyl-1-propanol dehydrogenation catalysts (Table 18).
Table 18 Dehydrogenation of 1-phenyl-1-propanol by suspended Pd(100) nanocubes and Pd(111) nanoctahedra.\(^a\)

\[
\begin{array}{c|c|c|c}
\text{Catalyst} & \text{Conversion (\%)} & \text{Selectivity (\%)} & \text{Ring Hydrog.} \\
& & \text{Propiophenone} & \text{Propyl benzene} & \text{Hydrog.} \\
\hline
\text{Pd (100) Nanocubes} & 64 & 83.6 & 16.1 & 0.3 \\
\text{Pd (111) Nanoctahedra} & 69 & 76.4 & 23.3 & 0.3 \\
\end{array}
\]

\(^a\) Performed with 0.1 mol% suspended nanoparticles at 200 °C for 1 h under 1 atm of H\(_2\), with each reaction run in duplicate. Conversion and selectivity were determined by Gas Chromatography.

\(^b\) Ring hydrogenation products include: 1-cyclohexyl-1-propanol; cyclohexyl ethyl ketone; 1-cyclohexenyl ethyl ketone

Unfortunately, the nanoparticles’ selectivity for propiophenone was universally poor. The hydrogenolysis product, propylbenzene, was the major side-product, though the ring hydrogenation side-products were also observed. It was recognized that the conversion was higher than had been previously observed; this was considered a consequence of the side-product, propylbenzene (b.p. 160 °C), actively distilling away during the reaction, promoting non-equilibrium conditions. Despite the poor selectivity, some qualitative conclusions were drawn concerning face specificity: the fact that the Pd(100) nanocubes provided the best selectivity for propiophenone, as compared to the Pd(111) nanoctahedra, tenuously suggests that the Pd(100) face better selects for 1-phenyl-1-propanol than the Pd(111).

Despite their poor selectivity, the Pd(100) nanocubes were investigated further to determine if their selectivity could be improved. It was decided to impregnate the
nanocubes on mesoporous silica (SBA-15) via wet impregnation (5 wt% Pd), with SBA-15 being selected for its defined pore size and high surface area. The expectation was, by invoking the phenomenon of metal-support effects,\textsuperscript{35} that the catalytic activity and selectivity of the nanocubes may be influenced and/or improved. To determine if the PVP stabilizer was responsible for affecting the nanoparticles’ selectivity for propiophenone, a portion of the impregnated catalyst was thermally treated at 280°C for 1.5 h. It has been reported in the literature that such thermal treatments will remove PVP from the surface of the nanoparticles.\textsuperscript{30,31} To determine if the nanoparticles were successful impregnated on the SBA-15, and if any morphological changes occurred during the thermal treatment, both catalysts were analyzed by TEM (Figure 46, Figure 47).

The TEM analysis revealed that the impregnation was quite successful; the nanocubes were thoroughly dispersed throughout the support. Unfortunately, while select nanoparticles did maintain their cubic structure (Figure 46-C), the majority did not. This was especially true after the thermal treatment, where absolutely no evidence of cubic nanostructures was observed (Figure 47). This was not entirely unexpected, however; as previously discussed, Pd(100) faces are the least thermodynamically stable face and are prone to surface reconstruction to minimize energy. For the SBA-15 supported nanocubes, the surface reconstruction was possibly a product of the wet impregnation procedure, or is evidence of the nanocubes’ inevitable fate. For the thermally treated supported nanocubes, the surface reconstruction was likely expedited by the thermal treatment itself.\textsuperscript{49,50} Interestingly, there was no evidence of significant particle
agglomeration or sintering, as the nanoparticles remained separate from one another on the surface of the support, and maintained their size at ~7-8 nm.

**Figure 46** TEM images of Pd(100) nanocubes impregnated on SBA-15 (average particle size: 7.5 nm).
Figure 47 TEM images of thermally treated Pd(100) nanocubes on SBA-15 (average particle size: 7 nm).
While it was clear that the supported Pd nanoparticles had not retained their surface specificity, for the sake of completion, both the SBA-15 supported Pd nanoparticles and the thermally treated SBA-15 supported Pd nanoparticles were used as catalysts in the dehydrogenation of 1-phenyl-1-propanol. As expected, the nanoparticles’ selectivity for propiophenone did not improve (Table 19). Again, the dominant side-product was propylbenzene, from the hydrogenolysis of 1-phenyl-propanol; and as before, the exceptionally high conversions were attributed to non-equilibrium conditions promoted by the loss of said side-product. There were concerns that the SBA-15 support itself was contributing to the poor selectivity observed, given that similar materials, such as zeolites, can catalyze some reactions (e.g. hydrocarbon cracking):\textsuperscript{51} however, when the dehydrogenation of 1-phenyl-1-propanol was attempted over SBA-15, only trace amounts of propylbezene were observed.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Propiophenone (%)</th>
<th>Propyl benzene (%)</th>
<th>Ring Hydrog. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15 Supported Pd Nanocubes</td>
<td>69</td>
<td>79</td>
<td>20.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Thermally Treated SBA-15</td>
<td>89</td>
<td>74.2</td>
<td>25.6</td>
<td>0.2</td>
</tr>
<tr>
<td>SBA-15 Supported Pd Nanocubes</td>
<td>69</td>
<td>79</td>
<td>20.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Performed with 0.1 mol% metal at 200 °C for 1 h under 1 atm of H\textsubscript{2}, with each reaction run in duplicate. Conversion and selectivity were determined by gas chromatography. \textsuperscript{b} Ring hydrogenation products include: 1-cyclohexyl-1-propanol; cyclohexyl ethyl ketone; 1-cyclohexenyl ethyl ketone.
Though this foray into surface specific Pd nanoparticles was not overly successful, the results did tenuously suggest that the Pd(100) face may better select for 1-phenyl-1-propanol dehydrogenation than the Pd(111) face, which is also supported by the literature. Consequently, a final, initial investigation was launched into the synthesis of Pd(100) nanocubes. To decrease the likelihood of surface reconstruction, thus potentially improving shape selectivity, it was decided to synthesize much larger Pd(100) nanocubes (> 16 nm), as had been observed during the TEM analysis of Pd/PEI·SiO$_2$ (Figure 31). Quite fortuitously, Xia et al. had published another procedure detailing the synthesis of Pd(100) cubes 18 nm in size.$^{28}$ Their methodology was adopted and repeated, the synthesized nanoparticles were washed and isolated by centrifugation, and then analyzed by TEM (Figure 48-Figure 49).

![Figure 48: Synthesis and TEM image of large Pd(100) cubes.](image)
Figure 49 TEM images of Pd(100) cubes (average particle size: 20 ± 2.4 nm).
The synthesis of large Pd(100) cubes was a success: the shape selectivity was essentially 100%, and the particle size was in excess of the desired 16 nm. The Pd(100) cubes’ catalytic activity and selectivity was tested via the dehydrogenation of 1-phenyl-1-propanol (Table 20).

**Table 20** Dehydrogenation of 1-phenyl-1-propanol by suspended Pd(100) cubes.$^a$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity$^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Propiophenone</td>
</tr>
<tr>
<td>Unsupported Pd(100) cubes</td>
<td>46</td>
<td>99.26 ± 0.04</td>
</tr>
</tbody>
</table>

$^a$ Performed with 0.1 mol% suspended nanoparticles at 200 °C for 1 h under 1 atm of H$_2$. Conversion and selectivity were determined by Gas Chromatography.

$^b$ Approximate value back-calculated from ICP-OES determined Pd concentration (Section 2.3.10)

$^c$ Hydrogenolysis product was the only side-product observed.

The selectivity exhibit by the Pd(100) cubes for propiophenone was very good, and strongly suggests that the Pd(100) face selects for the dehydrogenation of 1-phenyl-1-propanol. There was also no evidence of the ring hydrogenation side-products: only trace amounts of the hydrogenolysis product, propylbenzene, were observed. This suggests that it was the Pd(111) faces of the commercial Pd/SiO$_2$ catalyst that were catalyzing the ring hydrogenation pathways (Section 2.4.5, Table 15). The fact that propylbenzene was still observed suggests that the Pd(100) face does catalyze the hydrogenolysis pathway, just at significantly lower rates than the dehydrogenation pathway; or, the more reactive edge atoms of the cubes, due to their lower coordination
number, were responsible for catalyzing the reaction. If the hydrogenolysis pathway was being catalyzed by the edge atoms, it would explain why the propylbezene was only present in trace amounts: the sheer size of the cubes would keep the ‘concentration’ of edge atoms low by comparison.

To determine whether surface reconstruction occurred during the dehydrogenation reaction at 200 °C, the Pd(100) cubes were isolated from suspension by filtration through vulcanized carbon; the carbon was then sent for TEM analysis (Figure 50). It was evident from the TEM images that the Pd(100) cubes did not undergo surface reconstruction after exposure to 200 °C heat; this suggests that these Pd(100) cubes could maintain their structure and selectivity across multiple reactions.

These initial results with the Pd(100) cubes were very promising, however initial attempts to reproduce these results have not been successful: the nanoparticles were found to be inactive after several weeks of being suspended in either water or methanol. A fresh batch of Pd(100) cubes was equally unreactive. This suggests that the synthesis and maintenance of these cubes is very procedurally dependent, and a systematic approach to their production will have to be undertaken if these Pd(100) cubes are to be utilized as dehydrogenation catalysts. One possible explanation for the Pd(100) cubes loss and/or lack of catalytic activity is the bromide ion used as a surface stabilizer: bromide was selected for its penchant for interacting with the Pd(100) face, subsequently aiding in the growth of those faces. It is possible that the surface bromide migrated while the cubes are suspended and blocked the catalytically active sites. It is also possible, if not likely, that there is a fine balance to the amount of bromide that can be used for the
synthesis of the Pd(100) cubes before catalytic activity is lost: due to their electronegative
nature, halides can act as catalytic poisons.

Figure 50 TEM images of Pd(100) cubes on vulcanized carbon after exposure to 200 °C heat.
2.5 Conclusions and future work

This project’s objective was to optimize the dehydrogenation reaction of the proposed TRFC system: to identify a heterogeneous catalyst that could provide a selectivity of 99.0 - 99.9% for propiophenone, and remain robust under the TRFC’s dehydrogenation conditions. Pd/SiO$_2$ was chosen as that dehydrogenation catalyst due to its excellent selectivity (99.65%) and stability (Section 2.4.4). The ideal selectivity of $\geq 99.9\%$ was never realized however, even under idealized conditions where the catalyst could be pre-treated to remove possible surface adsorbed water (Section 2.4.4) or where surface-specific nanoparticles were used in place of the heterogeneous commercial catalyst (Section 2.4.7). Consequently, a concession had to be made that desired selectivities of $\geq 99.9\%$ for propiophenone are likely unattainable for the proposed TRFC system.

It was also recognized that it is unrealistic to expect the exceptionally high selectivity exhibited by Pd/SiO$_2$ (99.65%) to be readily reproduced across commercially synthesized catalyst lots. Three different lots of Pd/SiO$_2$ were used during the TRFC’s development, and each exhibited excellent selectivity for propiophenone, as confirmed by $^1$H NMR and/or GC analysis; a fourth lot later purchased from the same supplier exhibited selectivities of $98.6 \pm 0.1\%$ (GC analysis). And while it was not observed within the context of this work, there is also precedence for catalytic activity and selectivity to be influenced by sample heterogeneity within the same catalyst lot.

As such, while it has been demonstrated that Pd/SiO$_2$ can afford excellent selectivities and robustness for the dehydrogenation of 1-phenyl-1-propanol, if the
commercially available Pd/SiO$_2$ continues to be used as received, contingencies must be engineered into the TRFC system to compensate for the catalyst’s inherent heterogeneity: a selectivity no higher than 99.0% should be assumed when calculating the expected operational lifetime of the working fluid.

There are still investigative avenues available for increasing catalytic selectivity and/or decreasing catalytic heterogeneity. Investigation into the large Pd(100) cubes should continue. First, a method for reproducibly synthesizing and impregnating the Pd(100) cubes on a silica-based support would have to be developed. With an optimized synthetic procedure coupled with an optimized impregnation methodology, reproducible lots of supported Pd(100) cubes could then be produced, each with the same size and shape selectivity, and subsequently, the same catalytic activity and selectivity. Having that kind of reproducibility in a heterogeneous catalyst could be revolutionary, not just for the TRFC system, but for any system dependent on heterogeneous catalysis. Prior to their implementation in the TRFC system, however, the robustness of the supported Pd(100) cubes would have to be established in order to determine if they are resistant to Pd leaching and surface reconstruction in the face of the TRFC’s operating conditions.

Alternatively, the focus could shift to modifying the commercially available Pd/SiO$_2$ itself. There is much precedence in the literature for the modification of heterogeneous catalysts to influence their catalytic activity.$^{52,53}$ Select modification of the commercial Pd/SiO$_2$ catalyst might minimize some of the heterogeneity inherent between catalyst lots. By evoking the herein established face specificity for the dehydrogenation of 1-phenyl-1-propanol over Pd catalysts (Section 2.4.7), the Pd(111) faces of the
commercial Pd/SiO\textsubscript{2} could be selectively deactivated through the addition of dopants. Dopants known to selectively adsorb to the (111) faces of Pd and/or Pt were tentatively identified: Bi\textsubscript{2}O\textsubscript{3}, TeO\textsubscript{2} and alkylthiols.\textsuperscript{52,53} A method to reproducibly dope commercial Pd/SiO\textsubscript{2} could be developed and optimized, followed by a comprehensive, combinatorial investigation into various types and concentrations of Pd(111) selective dopants until one provided a high selectivity, reproducibly, across catalyst lots.

In conclusion, Pd/SiO\textsubscript{2} was identified as the best catalyst for the dehydrogenation reaction of the proposed TRFC system. It was demonstrated that Pd/SiO\textsubscript{2} could exhibit excellent selectivity and stability in the face of the TRFC’s operating conditions. Despite the high selectivity exhibited by Pd/SiO\textsubscript{2}, however, it has been suggested that the inherent heterogeneity of the catalyst system be taken into account when engineering the TRFC system: a selectivity no higher than 99.0% should be assumed when calculating the operational lifetime of the working fluid.
2.6 References

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(12) Kenner, D. Land Rover FAQ: Exhaust Gas Temperatures **2005**.


2.7 Appendix: Gas Chromatography Calibration Curves and Method

Three calibration curves were developed for 1-phenyl-1-propanol, propiophenone, and propylbenzene on a Shimadzu GC-17A with a flame ionization detector (FID), using an Agilent Technologies DB-5ms Ultra Inert column, length ~30 m, inner diameter 0.25 mm, film thickness 0.25 µm. The response ratio (integrated peak area of analyte peaks versus internal standard peak) was plotted versus the mass ratio (mass of analyte versus internal standard). A linear regression was performed for each curve with a forced intercept of (0,0) to determine the response factor, which was used to determine unknown quantities of analytes in product mixtures. The response factor for all byproducts was assumed to be the same as that measured for propylbenzene.

In each case, five stock solutions were prepared for analysis, each containing 100.0 µL (77.3 mg) of the internal standard measured by an adjustable micropipette. The analyte amount was varied from 0 to 1000 µL. The samples were dissolved in approximately 15 ml of HPLC-grade methanol. Exact concentrations are not required based on the internal standard methodology used. 150 µL of each solution was removed and placed into a second 4-dram vial and diluted with a further 15 ml methanol. The vials were capped and inverted 40 times before analysis.

The temperature profile of the GC method used for analyzing all stock and experimental solutions is delineated in Table X, where the injector and detector was held constant at 250 °C. Each stock and experimental GC sample was analyzed in triplicate, and compared to GC traces of the pure starting material and sample solvent to ensure that
each peak observed could be accurately identified as starting material, product, and/or side product.

Table 21 Dehydrogenation Oven/column temperature profile.

<table>
<thead>
<tr>
<th>Rate (°C/min)</th>
<th>Temp (°C)</th>
<th>Hold (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>70</td>
<td>0.0</td>
</tr>
<tr>
<td>15.0</td>
<td>90</td>
<td>1.0</td>
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<tr>
<td>10.0</td>
<td>120</td>
<td>2.0</td>
</tr>
<tr>
<td>10.0</td>
<td>230</td>
<td>1.0</td>
</tr>
<tr>
<td>40.0</td>
<td>70</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 22 Calibration curve data for 1-phenyl-1-propanol.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyte added (µL)</th>
<th>Mass (mg)</th>
<th>Mass Ratio</th>
<th>Mean Response Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0</td>
<td>0.0</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>B</td>
<td>250.0</td>
<td>248.5</td>
<td>3.215</td>
<td>3.022</td>
</tr>
<tr>
<td>C</td>
<td>500.0</td>
<td>497.0</td>
<td>6.429</td>
<td>5.977</td>
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<tr>
<td>D</td>
<td>750.0</td>
<td>745.5</td>
<td>9.644</td>
<td>8.604</td>
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<tr>
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<td>1000.0</td>
<td>994.0</td>
<td>12.86</td>
<td>11.26</td>
</tr>
</tbody>
</table>

Linear regression gives: response ratio = 0.890 (mass ratio) + 0.010 with an $R^2 = 0.999$. 
Table 23 Calibration curve data for propiophenone

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyte added (µL)</th>
<th>Mass (mg)</th>
<th>Mass Ratio</th>
<th>Mean Response Ratio</th>
</tr>
</thead>
<tbody>
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<td>0.000</td>
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<td>B</td>
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<tr>
<td>C</td>
<td>500.0</td>
<td>504.5</td>
<td>6.527</td>
<td>5.648</td>
</tr>
<tr>
<td>D</td>
<td>750.0</td>
<td>756.8</td>
<td>9.790</td>
<td>9.526</td>
</tr>
<tr>
<td>E</td>
<td>1000.0</td>
<td>1009.0</td>
<td>13.05</td>
<td>12.14</td>
</tr>
</tbody>
</table>

Linear regression gives: \( \text{response ratio} = 0.933 \times \text{mass ratio} + 0.017 \) with an \( R^2 = 0.999 \).

Table 24 Calibration curve data for propylbenzene

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyte added (µL)</th>
<th>Mass (mg)</th>
<th>Mass Ratio</th>
<th>Mean Response Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0</td>
<td>0.0</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>B</td>
<td>250.0</td>
<td>215.5</td>
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<tr>
<td>C</td>
<td>500.0</td>
<td>431.0</td>
<td>5.576</td>
<td>7.336</td>
</tr>
<tr>
<td>D</td>
<td>750.0</td>
<td>646.5</td>
<td>8.364</td>
<td>11.50</td>
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<tr>
<td>E</td>
<td>1000.0</td>
<td>862.0</td>
<td>11.15</td>
<td>15.67</td>
</tr>
</tbody>
</table>

Linear regression gives: \( \text{response ratio} = 1.38 \times \text{mass ratio} + 0.01 \) with an \( R^2 = 0.999 \).
2.8 Appendix: NMR Spectra of 1-(4-tertbutyl)phenyl-1-propanol

Figure 51 $^1$H NMR of 1-(4-tertbutyl)phenyl-1-propanol.
Figure 52 COSY of 1-(4-tertbutyl)phenyl-1-propanol.
Figure 53 HSQC of 1-(4-tertbutyl)phenyl-1-propanol.
Chapter 3

Heterocyclic functionalized siloxane polymers as H₂ storing liquids

3.1 Introduction

In response to the Hydrogen Initiative (Section 1.3), we proposed a H₂ storing liquid that incorporated the hydrogen-storing capacity of heterocycles with the thermal stability of polysiloxanes to generate polymethylpyridylsiloxanes as alternative energy carriers (Figure 54). As a hydrogen-storing liquid, the heterocyclic functionalized polymers were to be designed to meet the following criteria: quick, clean and reversible dehydrogenation; enthalpy of dehydrogenation at or below 50 kJ/mol to allow lowest possible dehydrogenation temperature; liquid and non-volatile between -40°C and dehydrogenation temperature; meet targets set by US DoE (Section 1.3); as well as being chemically and thermally stable at operating temperatures. Polymethyl(3-pyridyl)siloxanes would be synthesized to avoid any possible hydrolytic and hydrogenolytic cleavage that can result from N-C-N and N-C-Heteroatom linkages.

Figure 54  Structure of the proposed polymethyl(3-pyridyl)siloxanes.
We envisioned our alternative energy carrier being used in conjunction with the existing refueling infrastructure: the hydrogenated material would be pumped into cars at a refueling station, the H₂ would be released and used to power the vehicle via a fuel cell, and the dehydrogenated material would be off-loaded and re-hydrogenated at a factory. If successfully synthesized, the polymethyl(3-pyridyl)siloxanes would offer a hydrogen storing capacity of 4.2 wt%. This hydrogen-storing capacity does not meet the targets set by the US DoE, although it was expected that the thermal stability and high elasticity provided by the siloxane backbone would compensate for the difference.

3.2 Polysiloxanes

3.2.1 Physical and chemical properties

Polysiloxanes were chosen for this project specifically because of their unique thermal properties. Siloxanes are characterized by their elasticity at markedly low temperatures: they possess some of the lowest glass transition temperatures, \( T_g \) (i.e. -150 °C to -70 °C) and crystalline melting points, \( T_m \) (e.g. PDMS: -54 °C to -45 °C) known to polymer science. Siloxanes are equally characterized by their high thermal and thermo-oxidative stability: their ability to resist thermal degradation at temperatures greater than 300-350 °C lends them a 150-200 °C advantage over carbon-backbone based polymers, which usually decompose at 150-200 °C. The result is a polymer with an exceedingly vast liquid range (-150 °C to 350 °C), especially in comparison with other proposed hydrogen storing species such as pyridine/piperidine (-42 °C to 115 °C), benzene/cyclohexane (5.5 °C to 80 °C), and carbazole/dodecahydrocarbazole (74 °C to
350 °C) (Figure 55). This makes siloxanes a viable candidate for an alternative energy carrier in Canadian climates. While pyridine/piperidine does offer a liquid range that could be suitable for use in Canadian climates, it is a flammable liquid with a low flash point (17-18 °C). In contrast, polymethylsiloxanes are nonflammable with flash points that can exceed 300 °C, providing a fire-safe alternative to diesel/gasoline. The specific thermal properties of polysiloxanes are dictated by three structural characteristics: the Si-O bond; the alternating silicon and oxygen atoms within the polymer chain; and the type and arrangement of the siloxane backbone substituents. As the first two characteristics are inherent of polysiloxanes, it is expected that they will all share similar elastic and thermal properties, with any variations to those properties being due to their particular substituents.

Figure 55 A liquid range comparison between polysiloxanes and proposed hydrogen storing liquids. The blue dots represent the respective liquids’ flash points.
The Si-O bond is unique. As compared to C-X bonds, the Si-O bond is relatively long at $1.64 \pm 0.03 \text{ Å}$, but is shorter than the sum of the respective atomic radii. The Si-O bond possesses partial double bond character; this results from a partial overlap between the empty, low energy 3d orbitals of silicon and the 2p orbitals of oxygen. Oxygen back donates to the silicon, forming a $d_{π} - p_{π}$ link in addition to the expected $σ$ bond. The Si-O bond is also partially ionic due to the electronegativity difference between silicon (1.8) and oxygen (3.5); depending on the method of calculation, the bond’s ionic character can be as high as 51%. It is these unique bond characteristics that contribute to the stability and elasticity of polysiloxanes: the partial ionic and double bonded character lends siloxanes their thermo-oxidative stability; and the long bond length lends siloxanes their elasticity at low temperatures and conformational flexibility.

The alternating silicon and oxygen atoms along the siloxane backbone are also responsible for the flexibility observed in siloxanes. This flexibility results from the long Si-O bond lengths along the backbone, the long Si-C bond lengths of the substituents, and the alternating O-Si-O / Si-O-Si angles along the siloxane backbone. The longer Si-O bond lengths allow for maximum spatial separation of any organic substituents linked to the siloxane backbone, minimizing steric hindrance and congestion. Due to a lower barrier to linearization of approximately 1.3 kJ/mol, the Si-O-Si angle is comparatively wider than the O-Si-O angle, with the typical range being 140° – 150° for the former and 102° – 112° for the latter. This wider Si-O-Si bond angle results from the delocalization of the oxygen’s lone pair into the bonding space between the silicon and oxygen atoms, subsequently altering the $sp^3$ hybridization and widening the bonding angle. It is the
nature of the Si-O-Si angle that allows the siloxane backbone to contort in ways that would otherwise be impossible.

### 3.2.2 Environmental concerns

A siloxane-based energy carrier was proposed for this project, in part, because siloxanes are already used ubiquitously in our daily lives: they are found in commercial products such as cosmetics and deodorants, and medical products such as transdermal patches and implanted prosthetics devices.\(^4\)\(^5\) Fortunately, some of these siloxanes, particularly liquid silicones, can be converted back into cyclic oligosiloxanes via base or acid treatment to be recycled. Other siloxanes, such as polydimethylsiloxane (PDMS), are used in such a way that they do not lend themselves to recycling. Consequently, PDMS can find its way into rivers, ground water and soil; once there, the polymer (Me\(_3\)SiO-(Me\(_2\)SiO)\(_n\)-SiMe\(_3\)) can depolymerize into its monomer, HO-Si(Me\(_2\))-OH, which then breaks down into SiO\(_2\) and CO\(_2\). The whole process can take a few months or years to complete.\(^4\) Some siloxane oligomers, such as octamethylcyclotetrasiloxane and 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane (Figure 56), have shorter lifetimes in water and sediment, with half-lives on the order of days and months. These oligomers do have a moderate to high potential to bio-accumulate, however, and can affect aquatic life at very low concentrations (<0.1 mg/L); PDMS does not.\(^5\)^\(^6\) We, therefore, decided to model our proposed siloxanes against the longer-chained siloxanes with the hope that our alternative energy carrier would pose less of an environmental hazard.
3.2.3 The reason for pyridyl groups

Pyridyl groups were chosen as the hydrogen-storing moiety of our alternative energy carrier because of computational work done by Crabtree et al. Their focus was to determine a way to lower the prohibitively high dehydrogenation enthalpy of hydrocarbons such as cyclohexane. Computationally, Crabtree et al. investigated the effect of replacing cyclohexyl ring carbons (i.e. CH₂/CH) with nitrogens (i.e. NH/N) and found that there was a general downward trend in dehydrogenation enthalpies, as compared to cyclohexane (Table 25). Crabtree et al. then extended their computational studies to a wider array of N-heterocycles and amino-substituted benzenes and calculated the temperature at which each would dehydrogenate. They determined there was a general additive effect with respect to ring nitrogens or N-substituents: the more ring nitrogens and N-substituents, the lower the temperature of dehydrogenation (e.g. T_{benzene} = 599 K, T_{pyridine} = 546 K, T_{1,3-diazine} = 483 K, T_{1,3,5-triazine} = 436 K). By comparing the dehydrogenation temperatures of benzene (599 K), pyridine (546 K), and aniline (532 K), the authors postulated that a nitrogen containing substituent could be more effective at lowering the dehydrogenation temperature than a ring nitrogen. Pez et al.
have also shown, computationally and experimentally, that incorporation of heteroatoms into a cyclic hydrocarbon reduces the enthalpy of dehydrogenation.\textsuperscript{9}

As an extension of this work, Jessop, et al.\textsuperscript{10} tested, among other things, the effect of electron donating groups on the dehydrogenation/hydrogenation on N-heterocycles. They found that 4-aminopiperidine and piperidine-4-carboxamide readily and cleanly dehydrogenated at lower temperatures (i.e. 170 °C-220 °C), and that pyridine-4-carboxamide did readily and cleanly hydrogenate back to the piperidine. The authors noted however, that the hydrogenation of 4-aminopyridine resulted in the disproportionation product dipiperidin-4-ylamine (Figure 57), and that other amino substituted pyridine/piperidine pairs also underwent disproportionation during dehydrogenation and/or hydrogenation (e.g. 4-dimethylaminopiperidine). Having taken this previous research into consideration, we chose pyridine as the model hydrogen-storing moiety for our alternative energy carrier, with the potential of investigating substituted pyridines as well.

\[
\begin{align*}
\text{4-aminopyridine} & \xrightarrow{5 \text{ mol}\% \text{ Pd/C}} \text{dipiperidin-4-ylamine} \\
& \xrightarrow{70 \text{ bar H}_2, 125 \degree \text{C}, 18-24 \text{h}} \\
\end{align*}
\]

\textbf{Figure 57} Disproportionation product of 4-aminopyridine hydrogenation, dipiperidin-4-ylamine.\textsuperscript{10}
**Table 25** Computationally determined dehydrogenation enthalpies of N-heterocycles as compared to cyclohexane.\(^a,7\)

<table>
<thead>
<tr>
<th>Dehydrogenation Enthalpy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Cyclohexane" /></td>
</tr>
<tr>
<td><img src="image" alt="Pyridine" /></td>
</tr>
<tr>
<td><img src="image" alt="Pyrimidine" /></td>
</tr>
<tr>
<td><img src="image" alt="Pyrazine" /></td>
</tr>
<tr>
<td><img src="image" alt="Piperazine" /></td>
</tr>
<tr>
<td><img src="image" alt="Piperazine" /></td>
</tr>
</tbody>
</table>

\(^a\) Calculations performed at the DFT level using the 6-31++G** basis set
3.3 Polysiloxanes in hydrogen based energy systems

There is precedence for the use of siloxanes, and specifically N-heterocyclic substituted siloxanes, in hydrogen based energy systems. A prominent example is with regard to polymer electrolyte membrane fuel cells (PEMFC), where siloxanes functionalized with ‘proton carriers’ have been used as electrolytic membranes: imidazole, benzimidazole, and 1,2,3 triazole, as well as sulfonyl and styrene groups have all been used as ‘proton carrying’ substituents. An electrolytic membrane consisting of polydimethylsiloxane cross-linked to metals has also been reported. Heterocyclic functionalized polysiloxanes are of particular interest for electrolytic membranes as they facilitate proton conduction in anhydrous conditions, allowing the fuel cell to operate at temperatures above 100 °C. This is an improvement over Nafion® based PEMFCs in terms of operational temperatures. The proton conductivities of these siloxane electrolytic membranes, however, are still markedly lower than that of Nafion® (i.e. 0.02-0.1 S/cm vs. 0.2 S/cm).

There are also a number of patents delineating the use of siloxanes in hydrogen storage. Toseland et al. filed a patent detailing the dehydrogenation of an organic compound via a microchannel reactor, where the dehydrogenated material is liquid and the evolved H₂ is subsequently isolated. The ‘organic compound’ was defined as the hydrogenated forms of extended polycyclic aromatic compounds, extended π-conjugated compounds containing heteroatoms, and π-conjugated, carbon-backbone polymers. N-ethyl carbazole was the only species suggested in a representative dehydrogenation process, however. In 2005, Pez et al. patented a process for the storage and release of H₂ to be subsequently supplied to fuel cells; the H₂ was released through the reversible
hydrogenation / dehydrogenation of π-conjugated substrates. Of the substrates claimed, phenyl substituted silanes and phenyl-, tolyl-, naphthyl- and anthracyl-substituted siloxanes were included. The working examples, however, only included pyrene, coronene and coronene analogs, pentacene, decahydronaphthalene, carbazole and carbazole analogs. Ichikawa and Fukuoka patented a hydrogen storage and supply system for storing and feeding H₂. While the available patent information was limited, from the figures it was apparent that the organic liquids claimed for storing and releasing hydrogen included polyalkysilanes, polymethylphenylsiloxanes and their oligomers; no heterocyclic-functionalized siloxanes were listed. One patent by Zeldin in 1989, specifically detailed the use of polymethylpyridylsiloxanes and their N-oxide derivatives, but not for hydrogen storage. The author was patenting the polymers for use as inverse phase transfer catalysts.

3.4 The project’s objectives

The objective of this research was to evaluate the viability of the project: to determine whether polymethylpyridylsiloxanes could be readily synthesized, and if said polymethylpyridylsiloxanes could be rapidly and reversibly hydrogenated. If the project was found to be viable, reaction conditions would then be optimized and further project development would commence. If it was not found to be viable, further investigation into the project would cease.
3.5 Experimental

3.5.1 General

Experimental procedures involving air and/or water sensitive compounds were conducted in the absence of oxygen and water under an atmosphere of N\textsubscript{2} and/or Ar, via standard Schlenk methods. Unless otherwise specified, all reagents were purchased from chemical suppliers (e.g. Sigma Aldrich, Acros Organics, Alfa Aesar, Fisher Scientific, Strem) and used without further purification. All gases were obtained from Praxair. NMR spectra were collected at 300 K on a Bruker AV-300 or AV-400 spectrometer at 300 MHz or 400 MHz, respectively, and referenced relative to the deuterated solvents’ residual proton-containing solvent signal. Solvents were dried by being passed over alumina in a solvent purification system, unless otherwise specified below. Molecular sieves were activated by being heated to > 100 °C in an oven for at least 7 days, and were stored in a glove box until use.

3.5.2 Synthesis of the monomer dichloromethylpyridylsilane

This procedure was adapted from the literature.\textsuperscript{19–21} Dry ether (200 mL) from a solvent purification system was added to a flame-dried 500 mL round bottom flask and stored over molecular sieves under an Ar atmosphere. 3-Bromopyridine (0.48 mL, 0.005 mol) was added to a flame-dried, 250 mL 2-neck round bottom flask with stir bar and dissolved in ether (80 mL) under an Ar atmosphere. Phenyl magnesium bromide (17 mL, 3M in ether, 0.05 mol) was added drop wise, with stirring, over 15 min under an Ar
atmosphere. The reaction mixture was stirred for 1 h, during which the product, pyridyl magnesium bromide, precipitated. The pyridyl magnesium bromide was isolated by cannula filtration, washed three times with ether (total: 70 mL), and stored at 5 °C under Ar until use. The pyridyl magnesium bromide was then suspended in dry ether (30 mL), and added drop wise by cannula transfer to a flame-dried, 250 mL round bottom flask containing trichloromethylsilane (12 mL, 0.1 mol) dissolved in dry ether (40 mL), with stirring under an Ar atmosphere. The reaction mixture was stirred overnight at room temperature. The solvent and excess volatile reagents were removed under vacuum to reveal a yellow powder. A distillable liquid was expected. 21 1H NMR analysis revealed that the expected product, dichloropyridylsilane, had not been isolated.

3.5.3 General procedure for the synthesis of cyclic polymethyl(3-pyridyl)siloxane trimers

This procedure was adapted from the literature. 20, 21 Dry ether (300 mL) and dry THF (300 mL) from a solvent purification system were each added to a flame dried 500 mL round bottom flask and stored over molecular sieves for 5 days under an Ar atmosphere. The ether (40 mL) was added to a flame-dried 100 mL round bottom flask and cooled to -78 °C with an acetone/dry ice bath. n-Butyl lithium (8.8 mL, 2.5 M in hexanes, 0.022 mol) was added to the ether with stirring, via an Ar flushed needle and syringe. To this solution, 3-bromopyridine (1.93 mL, 0.02 mol) was added drop wise. The reaction mixture stirred at -78 °C for 1.5 h, allowed to warm to -20 °C for 1.5 h, and cooled back down to -78 °C. This reaction mixture was then cannula transferred under Ar into a flame-dried 250 mL round bottom flask containing trichloromethylsilane (19 mL,
0.16 mol) dissolved in ether (40 mL), and cooled to -78 °C. Once the transfer was complete, the reaction mixture was left to stir and allowed to warm up to room temperature overnight. The solvents and other volatile components were then removed under vacuum, and the mixture was dissolved in dry THF (40 mL). Zinc oxide (ZnO, 2.44 g, 0.03 mol), oven dried for at least 2 h at 120 °C, was then added to the reaction mixture with stirring under an atmosphere of Ar. This final mixture was allowed to stir at room temperature overnight, after which it was basified (pH 8) with sodium hydroxide. The product isolation method of choice was extraction. Using a separatory funnel, the reaction mixture was extracted three times with a total volume of 150 mL of organic solvent (dichloromethane or ether). The organic layer was isolated and dried over MgSO₄; the solvent removed under vacuum. Three separate reactions were attempted, each with subtle modifications to the general procedure above. First synthesis: trimethoxymethylsilane was used in place of trichloromethylsilane, and ZnO was first suspended in THF prior to addition via cannula transfer. Second synthesis: the reaction mixture was added to a round bottom flask containing ZnO suspended in THF with stirring. Third synthesis: the ZnO was added all at once, as a solid, via an addition funnel. These syntheses were not successful in generating intended product, cyclic polymethyl(3-pyridyl)siloxane.

3.5.4 General procedure for the synthesis of trimethylsilyl terminated polymethyl(3-pyridyl)siloxane tetramer

This procedure was adapted from the literature. Potassium phosphate (K₃PO₄) was dried in the oven at 100 °C. 3-Iodopyridine was stored in a calcium chloride desiccator.
The rhodium catalyst \([\text{RhCl(CO)(PPh}_3]_2\) was stored in the glove box under inert atmosphere. N-Methyl-2-pyrrolidone was dried over molecular sieves for 5 days and degassed before being stored in the glove box. \(\text{K}_3\text{PO}_4\) (1.27 g, 0.006 mol), 3-iodopyridine (0.82 g, 0.004 mol), and \(\text{RhCl(CO)(PPh}_3)_2\) (0.138 g, 0.0002 mol, 5 mol% relative to 3-iodopyridine) were weighed out in the glove box and added to an oven dried 45 mL pressure tube with a stir bar. N-Methyl-2-pyrrolidone (6 mL) was added to the mixture with stirring, and then stored in the glove box freezer at -16 °C for 10 min. Polymethylhydrosilane (0.46 mL, 0.001 mol) was added drop wise to the cooled solution and left to stir overnight at room temperature in the glovebox. The capped pressure tube containing the reaction mixture was moved out of the glove box and into the fumehood where it was heated for 48 h at 65 °C, then left stirring at room temperature for 5 days. The reaction was quenched with deionized water. Attempts at product isolation included vacuum distillation over 72 h at a maximum temperature of 180 °C, and small-scale extractions that involved 0.2-0.3 mL of the reaction mixture and 2 mL of deionized water. Pure product could not be isolated. The crude product mixture was a clear orange-brown liquid, and was analyzed by NMR spectroscopy and low resolution EI-MS (LR EI-MS). \(^1\text{H NMR}\) 0.00 - 0.17 (m, 25 H, \(\text{H}^{\text{SiCH}_3}\)), 7.09 (dd, \(J=7.9\), 4.8 Hz, 4 H, \(\text{H}^5\)), 8.00 (d, \(J=7.8\) Hz, 4 H, \(\text{H}^4\)), 8.55 (d, \(J=4.6\) Hz, 4 H, \(\text{H}^6\)), 8.83 ppm (s, 4 H, \(\text{H}^2\)). HSQC \(^{13}\text{C}:\) 1.8 \(\text{C}^{\text{SiCH}_3}\), 125.3 \(\text{C}^5\), 144.1 \(\text{C}^4\), 147.9 \(\text{C}^6\), 155.7 ppm \(\text{C}^2\). LR EI-MS: 520 m/z corresponding to fragment \(\text{C}_{23}\text{H}_{28}\text{N}_4\text{O}_3\text{Si}_4\).
3.5.5 Synthesis of 3-trimethylsilylpyridine

Magnesium (Mg) metal (1.34 g, 0.055 mol) was polished with steel wool, washed in a 20% HCl solution, rinsed with water and acetone, and flame dried in a 250 mL round bottom flask under vacuum, and then stored under an atmosphere of N₂. Tetrahydrofuran (THF), dried via a solvent purification system, was added to the Mg-containing round bottom flask (40 mL). While under a N₂ atmosphere, the round bottom flask was fitted with a stir bar, a water-cooled condenser and connected to a N₂ bubbler. Under a N₂ atmosphere, 3-bromopyridine (4.8 mL, 0.05 mol) was added carefully and dropwise to the mixture, which required heating between 60-70 °C to initiate reaction. The mixture was stirred for 24 h under a N₂ atmosphere under reflux. Trimethylsilyl chloride (6.4 mL, 0.05 mol) was then added dropwise over several minutes, and the mixture was stirred under a N₂ atmosphere at room temperature for another 24 h. Once the reaction was complete, the THF was removed under vacuum, the product mixture was dissolved in dichloromethane, and then washed with deionized water (200 mL) via extraction. The organic layer (CH₂Cl₂) was isolated and dried over magnesium sulfate, and the solvent removed under vacuum. The presence of the desired product was confirmed by ¹H NMR (solvent: CDCl₃). The product was purified by vacuum distillation at 70 °C (0.6 mbar). Isolated, purified yield: 17% (clear orange-yellow liquid). ¹H NMR: 0.29 (s, 9H, H⁵CH₃), 7.23 (ddd, J=7.5, 4.9, 1.0 Hz, 1 H, H³), 7.76 (ddd, J=7.5, 1.8 Hz, 1 H, H⁴), 8.56 (dd, J=4.9, 1.8 Hz, 1 H, H²), 8.67 ppm (dd, J=1.6, 1.0 Hz, 1 H, H⁵). This corresponds to literature values: 0.29 (s, 9H, H⁵CH₃), 7.23 (ddd, 1 H), 7.76 (ddd, 1 H), 8.57 (dd, 1 H), 8.67 ppm (dd, 1 H).²⁴ See Section 3.9: Appendix for select NMR spectra.
3.5.6 General procedure for the hydrogenation of 3-trimethylsilylpyridine to 3-trimethylsilylpiperidine

3-Trimethylsilylpyridine (100 mg, 6.6 x 10⁻⁴ mol) was placed in a 3-dram vial fitted with a stir bar, and dissolved in 3 mL ethyl acetate. A heterogeneous catalyst, Pd/C or Rh/C, was then added to the mixture (5 mol % loading). The vial containing the reaction mixture was then immediately placed in a 31 mL high pressure Parr vessel, and the headspace purged with H₂ (5.0 purity). Under a H₂ atmosphere, the reaction mixture was brought to temperature, with stirring at 650 rpm. Once at temperature, the Parr vessel was pressurized to 70 bar H₂, and the mixture left to react. After the reaction was complete, the Parr vessel was cooled to room temperature and vented. The product mixture was isolated from the catalyst via gravity filtration through a pipette fitted with a Kimwipe® plug, and the solvent removed under vacuum. Five investigative trials were run, varying time, temperature and catalyst (Table 26). The product mixture from the best trial was evaluated by 1-D (¹H) and 2-D (COSY, HSQC) NMR, as well as high-resolution electron impact mass spectrometry (HR EI-MS). The % conversion and selectivity was calculated from the integrations of the ¹H NMR spectrum of each trial. The isolated product was a clear yellow liquid. ¹H NMR: -0.05 (s, 9 H, H₃SiCH₃), 0.83 (tt, J=12.6, 3.4 Hz, 1 H, H'), 1.19 - 1.29 (m, 1 H, H₃), 1.45 (qt, J=12.6, 3.9 Hz, 1 H, H₅), 1.59 - 1.67 (br m, 1 H, H₅'), 1.72 - 1.81 (br d, 1 H, H'), 2.49 (dd, J=12.4 Hz, 1 H, H₅), 2.59 (ddd, J=12.3, 2.8 Hz, 1 H, H₆), 3.06 ppm (br t, J=12.8 Hz, 2 H, H₃²/₆'). HSQC (¹³C): -3.6 (C₃SiH₃), 25.6 (C₄), 26.8 (C₃), 27.8 (C₅), 47.2 (C₆), 48.2 ppm (C²). HR EI-MS: C₈H₁₉NSi, 157.1281 m/z (measured), 157.1287 m/z (calculated). See Section 3.9: Appendix for select NMR spectra.
3.5.7 Optimized procedure for the hydrogenation of 2-trimethylsilylpyridine

This procedure was previously described in Dominique Vanier’s honors thesis.\textsuperscript{38} 2-Trimethylsilylpyridine was purchased and used as received from Sigma Aldrich. 2-Trimethylsilylpyridine (100 mg, $6.6 \times 10^{-4}$ mol) was placed in a 3-dram vial fitted with a stir bar, and dissolved in 3 mL ethyl acetate. A heterogeneous catalyst, Rh/C, was then added to the mixture (5 mol % loading). The vial containing the reaction mixture was then immediately placed in a 31 mL high pressure Parr vessel, and the headspace purged with H\textsubscript{2} (5.0 purity). Under a H\textsubscript{2} atmosphere, the reaction mixture was brought to temperature (75 °C), with stirring at 650 rpm. Once at temperature, the Parr vessel was pressurized to 70 bar H\textsubscript{2}, and the mixture left to react for 48 h. After the reaction was complete, the Parr vessel was cooled to room temperature and vented. The product mixture was isolated from the catalyst via gravity filtration through a pipette fitted with a Kimwipe\textsuperscript{®} plug, and the solvent removed under vacuum. The best trial afforded the product, a clear yellow liquid, with 100% conversion and selectivity, quantitatively. It was evaluated by \textsuperscript{1}H NMR (Acetone-$d_6$): -0.02 (s, 9 H), 1.23 - 1.32 (m, 2 H, CH\textsubscript{2}), 1.33 - 1.44 (m, 1 H, CH\textsubscript{2}), 1.51 - 1.59 (br. m, $J=10.5$ Hz, 2 H, CH\textsubscript{2}), 1.76 - 1.83 (m, 1 H, CH\textsubscript{2}), 2.00 - 2.09 (m, 1 H, NCH-Si), 2.48 - 2.57 (ddd, $J=11.7, 2.5$ Hz, 1 H, NCH\textsubscript{2}), 2.97 - 3.04 ppm (br. m, 1 H, NCH\textsubscript{2}). The \textsuperscript{1}H NMR analysis of another hydrogenation trial (conversion: ~50%; selectivity: 100%) was performed in CDCl\textsubscript{3}, however, and its chemical shifts were found to be comparable to the spectrum of the best trial, despite the difference in deuterated solvent: -0.08 (s, 9 H) 1.20 - 1.30 (m, 2H, CH\textsubscript{2}), 1.31 - 1.44 (m, 1 H, CH\textsubscript{2}), 1.45 - 1.59 (br. m, $J=10.5$ Hz, 2 H, CH\textsubscript{2}), 1.69 - 1.77 (m, 1 H, CH\textsubscript{2}), 2.45 - 2.55 (ddd, $J=11.7, 2.5$ Hz, 1 H, NCH\textsubscript{2}) 2.97 - 3.05 ppm (br. m, 1 H, NCH\textsubscript{2}). Some peaks are
missing or broadened due to interference from the reaction solvent. The \(^1\)H NMR spectrum of crude 2-trimethylsilylpiperidine has been reported in the literature, and it was recorded in CDCl\(_3\) at 500 MHz.\(^{25}\) The reported literature values are as follows: -0.06 (s, 9 H, H\(^{SiCH_3}\)), 1.24-1.29 (m, 2 H), 1.38 - 1.41 (m, 1 H), 1.51 - 1.57 (m, 2 H), 1.74 - 1.77 (m, 1 H), 1.97 - 1.99 (m, 1 H), 2.49 - 2.55 (m, 1 H) 3.02 - 3.05 ppm (m, 1 H).\(^{25}\) The experimental values fall within the range of the reported literature values, and thus were considered to be in agreement.

### 3.5.8 Procedure for the dehydrogenation of 2-trimethylsilylpyridine

This procedure was previously described in Dominique Vanier’s honors thesis.\(^{38}\) 2-Trimethylsilylpyridine (300 mg, 0.0012 mol) and Rh/C (1 mol % loading) were added to a 50 mL round-bottom, fitted with a water condenser and gas bubbler. The reaction was stirred at 150 °C for 20 h while refluxing under a dynamic flow of Ar. A sample of the reaction mixture was analyzed by \(^1\)H NMR spectroscopy, which established 0% conversion after 20 h. The temperature was decreased to 130°C to prevent material loss and refluxed for an additional 24 h. The reaction mixture was analyzed by \(^1\)H NMR spectroscopy, which established complete material loss.

### 3.5.9 General procedure for the synthesis of 1,1,3,3-tetramethyl-1,3-(3-pyridyl) siloxane

3-Bromopyridine (3.6 mL, 0.0375 mol) was added to dry ether (85 mL, obtained from a solvent purification system and stored over molecular sieves) in a flame-dried, 2-neck
250 mL round bottom flask with a stir bar. The system was cooled to -78 °C via an acetone/dry ice bath and maintained under an Ar atmosphere. n-Butyl lithium (18.75 mL, 1.6 M in hexanes, 0.03 mol) was then added dropwise to the stirred solution from an Ar flushed needle and syringe, and the mixture was allowed to stir for 2 h at -78 °C. 1,1,3,3-Tetramethyl-1,3-dichlorosiloxane (2.9 mL, 0.015 mol) was dissolved in 4 mL of dry ether, cooled to -78 °C, and added dropwise to the reaction mixture. The mixture was stirred for an additional 2 h at -78 °C, and then warmed slowly to room temperature over the course of several hours. Once at room temperature, the reaction was filtered through an oven dried Celite™ bed. The reaction mixture’s round bottom flask and the Celite™ bed were rinsed with an additional 180 mL of ether to ensure product collection. The solvent was removed under vacuum and the remaining residue was triturated overnight with pentane (30 mL). The desired product dissolved into the pentane fraction, and was isolated by removing the solvent under vacuum. The product was analyzed by NMR spectroscopy. Isolated crude yield: 38% (clear orange-yellow oil). ¹H NMR: 0.38 (s, 12 H, H\text{SiCH}_3), 7.26 (ddd, J=7.5, 4.9, 0.8 Hz, 2 H, H\textsuperscript{3}), 7.77 (br. ddd, J=7.5, 1.8 Hz, 2 H, H\textsuperscript{3}), 8.61 (br. dd, J=4.9, 1.9 Hz, 2 H, H\textsuperscript{3}), 8.70 ppm (br d, J=1.0 Hz, 2 H, H\textsuperscript{2}). HSQC (\textsuperscript{13}C): 0.4 (C\text{SiCH}_3), 122.9 (C\textsuperscript{5}), 140.5 (C\textsuperscript{4}), 150.3 (C\textsuperscript{6}), 153.9 ppm (C\textsuperscript{2}). HSQC (\textsuperscript{29}Si): -0.54 ppm, correlating to the pyridine ring protons. HR EI-MS: C\textsubscript{14}H\textsubscript{20}N\textsubscript{2}OSi, 288.1122 m/z (measured), 288.1114 m/z (calculated). This corresponds to literature values: 0.38 (s, 12 H), 7.26 (m, 2 H), 7.76 (dt, 2 H), 8.58 (dd, 2 H), 8.68 ppm (s, 2 H).\textsuperscript{26} See Section 3.9: Appendix for select NMR spectra.
3.5.10 General procedure for the purification of 1,1,3,3-tetramethyl-1,3-(3-pyridyl) siloxane by vacuum distillation

This procedure was adapted from the literature. The crude product was placed in a 50 mL round bottom, which was then attached to a vacuum condenser fitted with a 50 mL receiver round bottom flask. The entire distillation apparatus was then connected to a Schlenk line, which was connected to a high vacuum pump. The crude product was put under vacuum (1 mbar) at room temperature with stirring to remove any volatile materials for 1 hour. After the first hour, the temperature was steadily raised over 12 h to 115 °C-220 °C (range of maximum temperatures investigated over several syntheses), and held at that maximum temperature for a minimum of 6 h. Any collected distillate was analyzed by NMR spectroscopy. If no distillate was collected, the initially crude product was analyzed by NMR spectroscopy to determine purity.

3.5.11 General procedure for the purification of 1,1,3,3-tetramethyl-1,3-(3-pyridyl) siloxane by chromatography

Chromatography was attempted, following a procedure outlined in the literature with silica as the packing material and ethyl acetate as the eluent. This procedure was first tested by thin layer chromatography (TLC): a small amount of the crude product was added neat to a silica TLC plate via a capillary tube. The plate was then placed in a screw-top jar containing ethyl acetate. The ethyl acetate was drawn up the length of the plate and the plate was removed when the solvent front was within a half centimeter to the top. After allowing the plate to dry, it was viewed under a UV lamp. This established
that two components were present on the plate, one that moved with the eluent and another that did not. Methanol was used to move the second component up the length of the plate. A larger scale test was performed in place of preparatory TLC to analyze the two components by NMR spectroscopy. The larger test was performed as follows: a short stem pipette was fitted with a Kimwipe® plug and filled with a silica plug 4 cm high. The test column was washed with ethyl acetate, after which 100 mg of the crude product was added to the top of the test column. The test column was washed with 10 mL ethyl acetate, followed by 10 mL methanol. Each aliquot was collected, the solvent removed under vacuum, and the isolated product analyzed by NMR spectroscopy. Pure product was not isolated. A second larger scale test was performed in place of preparatory TLC involving basic alumina (6 cm plug) as the packing material and chloroform as the eluent (30 mL). Three distinct bands were observed moving through the test column. A total of 10 separate aliquots were collected, including each band. The solvent was removed from each aliquot under vacuum, and each was analyzed for purified product. Pure product was not isolated.

3.5.12 General procedure for the hydrogenation of 1,1,3,3-tetramethyl-1,3-(3-pyridyl) siloxane

1,1,3,3-Tetramethyl-1,3-(3-pyridyl) siloxane (200 mg, 6.9 x 10^{-4} mol) was placed in a 3-dram vial fitted with a stir bar, and dissolved in 3 mL ethyl acetate or 2-butanol. A heterogeneous catalyst, Pd/C or Rh/C, was then added to the mixture (5 mol % loading). The vial containing the reaction mixture was then immediately placed in a 31 mL high pressure Parr vessel, and the headspace purged with H_2 (5.0 purity). Under a H_2
atmosphere, the reaction mixture was brought to temperature, with stirring at 650 rpm. Once at temperature, the Parr vessel was pressurized to 70 bar H₂, and the mixture left to react. After the reaction was complete, the Parr vessel was cooled to room temperature and vented. The product mixture was isolated from the catalyst via gravity filtration through a pipette fitted with a Kimwipe© plug, and the solvent removed under vacuum.

Four investigative trials were run varying time, temperature and catalyst (Table 27). The product mixture from the best trial was evaluated by 1-D (¹H) and 2-D (COSY, HSQC) NMR spectroscopy, as well as high-resolution electrospray mass spectrometry (HR ESI-MS). The % conversion was calculated from the integrations of the ¹H NMR spectrum of each trial. ¹H NMR: -0.01 - 0.15 (m, 27 H, H⁵(CH₃)), 0.80 - 1.02 (m, 2 H, H³), 1.26 - 1.33 (m, 2 H, H⁴), 1.42 - 1.57 (m, 2 H, H⁵), 1.64 (m, 2 H, H⁶), 1.80 (br. d, J=12.95 Hz, 2 H, H⁴'), 2.47 - 2.70 (m, 4 H, H²/⁶), 3.04 - 3.22 ppm (m, 4 H, H²'/⁶'). HSQC (¹³C): -1.4 (C(CH₃)), 25.1 (C⁴), 27.5 (C⁵), 28.3 (C³), 46.9/47.4 ppm (C²/⁶). HMBC (²⁹Si): 6.4 ppm (Si(CH₃), with correlations to H²-H⁴), -21.2 (Si(CH₃)). HR EI-MS: See Section 3.6.6. See Section 3.9: Appendix for select NMR spectra.
3.6 Results and discussion

It was decided that a three-pronged approach would be the most efficient in determining the validity of the project: the direct synthesis of polymethyl(3-pyridyl)siloxanes; the synthesis of methyl(3-pyridyl)siloxane oligomers; and, if necessary, the synthesis of silylated pyridines and/or bis(pyridyl)siloxanes as smaller analogues of polymethyl(3-pyridyl)siloxanes.

3.6.1 The first approach: synthesis of polymethyl(3-pyridyl)siloxanes

The synthesis of polymethyl(3-pyridyl)siloxanes has been previously documented in the literature (Figure 58).\textsuperscript{21} A modified synthesis was preemptively designed from various literature sources\textsuperscript{19–21} to avoid complications that can arise from lithium-halogen exchanges with 3-bromopyridine (Figure 59).\textsuperscript{28,29} The first step in the synthesis involved a Schlenk equilibrium reaction between phenylmagnesium bromide and 3-bromopyridine (10:1) to produce the pyridylmagnesium bromide reagent and bromobenzene as by-product.

\[ \text{HO}-\left(\frac{\text{Si}-\text{O}}{\text{Py}}\right)_n \xrightarrow{\text{n-BuLi}} \text{Cl}-\left(\frac{\text{Si}-\text{Cl}}{\text{Cl}}\right) \xrightarrow{i) \text{H}_2\text{O}} \xrightarrow{\text{ii) NH}_3(aq)} \]

**Figure 58** Procedure for the synthesis of polymethyl(3-pyridyl)siloxanes.\textsuperscript{21}
The pyridylmagnesium bromide was expected to precipitate out of solution as a white crystalline solid, allowing it to be easily isolated from the reaction mixture by filtration, and stored under inert atmosphere for further use. Such copious amounts of precipitate formed, however, that the reaction mixture became a slurry. It was inferred, based on the reagents used and the grey-white color of the precipitate, that magnesium oxide was likely formed as a byproduct. As there were no apparent means of selectively separating the desired pyridylmagnesium bromide from the resulting precipitate without compromising it, the precipitate was isolated and used without further purification. It was not expected that the presence of MgO would inhibit the subsequent step in the synthesis: the formation of the dichloromethylpyridylsilane monomer. The second step in the synthesis involved suspending the isolated precipitate in diethyl ether with a tenfold excess of trichloromethylsilane to favor mono-coupling between the Grignard reagent and trichloromethylsilane (Figure 59). The reaction was left stirring overnight; it was reported in the literature that the expected dichloromethylpyridylsilane monomer was

\[
\text{Figure 59 Modified synthesis of polymethyl}(3\text{-pyridyl})\text{siloxanes.}^{19-21}
\]

\[
\text{Figure 59 Modified synthesis of polymethyl}(3\text{-pyridyl})\text{siloxanes.}^{19-21}
\]
soluble in organic solvents, and as such, was expected to dissolve into the solvent as it formed.\textsuperscript{21} Subsequently, the liquid phase of the reaction mixture was isolated from the solid phase by cannula filtration, and the volatiles were removed under vacuum. The isolated liquid and solid residuals were stored separately under Ar. The liquid was analyzed by $^1$H NMR spectroscopy; the expected aromatic proton signals of the desired monomer were not observed.

It was reported in the literature that MgO could possess Lewis acidic sites and coordinate with pyridine.\textsuperscript{30} It was therefore hypothesized that the Lewis basic pyridyl ring of the monomer may have coordinated with the Lewis acidic MgO, thus preventing the monomer’s successful isolation. To test this hypothesis, the residual solid from the dichloromethylpyridylsilane monomer synthesis was washed in dry triethylamine. Triethylamine ($pK_{\text{aH}} = 10.8$) is a stronger base than pyridine ($pK_{\text{aH}} = 5.2$) and other substituted pyridines (e.g. 3-methylpyridine, $pK_{\text{aH}} = 5.7$).\textsuperscript{29,31} It was expected that, if the monomer was in fact coordinated to the surface of the residual solid, it would be displaced in favor of the more basic triethylamine, thus allowing the monomer to be isolated. Unfortunately, the monomer was not isolated. Had it been, the monomer would have been purified by vacuum distillation, polymerized by hydrolysis, and end-capped with chlorotrimethylsilane to form the desired polymethyl(3-pyridyl)siloxane (Figure 59).

It was therefore concluded that continuing this approach for testing the validity of polymethyl(3-pyridyl)siloxanes as hydrogen-storing liquids would not be advantageous. It was recognized that the efficient synthesis of high molecular weight polymers, and the characterization thereof, is not a trivial undertaking, and that the project would be better
served by investigating smaller analogues that would likely be easier to synthesize and characterize.

3.6.2 The second approach: synthesis of a cyclic polymethyl(3-pyridyl)siloxane trimer

The initial investigation into cyclic polymethyl(3-pyridyl)siloxane trimers was commenced by post-doctoral fellow Dr. Yi Cui of the Jessop group. Dr. Cui developed a cyclic trimer synthesis based upon reports in the literature (Figure 60).\(^ {20,21} \) The synthesis used zinc oxide (ZnO) as the cyclization reagent/oxygen supply. The reaction with ZnO was expected to proceed with the following stoichiometry (Equation 20):

\[
\text{ZnO} + \text{CH}_3\text{PySiCl}_2 \rightarrow \text{ZnCl}_2 + \frac{1}{3} [\text{CH}_3\text{PySiO}]_3
\]

Equation 20 The dichloromethyl(3-pyridyl)silane cyclization reaction with ZnO.\(^ {20} \)

![Synthesis of the cyclic polymethyl(3-pyridyl)siloxane trimer.](image)
Dr. Cui’s general synthesis involved the in situ synthesis of the dichloromethylpyridylsilane monomer, which was accomplished by a lithium halogen exchange with 3-bromopyridine, followed by ‘quenching’ with a ten-fold excess of trichloromethylsilane. As previously discussed (Section 3.6.1), an excess of trichloromethylsilane was used to favor a mono-coupling between the 3-lithiopyridine and trichloromethylsilane. Diethyl ether was used as solvent to favor the lithium halogen exchange over nucleophilic addition by the alkyllithium reagent.\textsuperscript{28,29} The monomer was isolated from volatile constituents under vacuum, and reacted with ZnO suspended in tetrahydrofuran (THF). Due to the poor solubility of ZnO in THF, the reaction was left stirring overnight, and then basified with aqueous sodium hydroxide (NaOH) to neutralize the zinc dichloride (ZnCl\textsubscript{2}) generated during the cyclization. Dr. Cui isolated the product by extraction, but only partially characterized it by \textsuperscript{1}H NMR and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS; repeat unit of 137 m/z). As such, it was necessary to repeat the synthesis in order to isolate and fully characterize the siloxane trimer. When attempting to repeat this synthesis, however, it was found to be highly dependent on the type of reagent used and the order of reagent addition; three syntheses were attempted to establish the optimal reagents and order of addition.

The first synthesis exchanged trichloromethylsilane with trimethoxymethylsilane for the in situ synthesis of the monomer. The motivation behind this exchange was to avoid any possible formation of hydrochloric acid from the infiltration of water into the system, and the subsequent pyridine ring protonation that could result. The major product isolated from this first synthesis was not the desired trimer, however, but a methoxy-
functionalized species, as evidenced by an intense singlet integrating to 3 H at 3.4 ppm in the $^1$H NMR spectrum. The structure of the unexpected product was not completely elucidated, however it is considered likely that the product was a methoxy-functionalized methylsiloxane.

The synthesis was then repeated with trichloromethylsilane in place of trimethoxymethylsilane. The monomer was formed *in situ* and then added dropwise to a stirring suspension of ZnO in THF; the resulting product was a granular solid that was insoluble in any solvent. It was suggested that, if water had infiltrated the system, hydrochloric acid may have formed from the partial hydrolysis of trichloromethylsilane, the pyridyl rings may have been protonated, and the insoluble solid may be a pyridinium salt that survived the basification step, or had only been partially deprotonated. This theory was taken into consideration, and a basic reflux was carried out using sodium carbonate (Na$_2$CO$_3$) and THF. If the theory was correct, the sodium carbonate would deprotonate the product during reflux, and the product would then be extracted into the THF and readily isolated. The system refluxed four days; no polymer was isolated.

In response to the failed second reaction, a final synthesis was attempted with one modification: ZnO was added *to* the dichloromethylpyridylsilane monomer all at once, given that the previous method/order of reagent addition had failed to produce any isolable product. A solvent-soluble product was isolated by extraction, however $^1$H NMR analysis showed a proliferation of unknown side products. No attempt to further purify the product was made. A discussion with Dr. Guojun Liu, a polymer chemist at Queen’s chemistry, made it evident that a successful polymer synthesis is dependent on the isolation and polymerization of a *pure* monomer. Given the lack of success in both
isolating a dichloromethylpyridyilsilane monomer (Section 3.6.1), and manipulating one in situ, a new approach was sought.

3.6.3 The second approach continued: synthesis of trimethylsilyl terminated polymethyl(3-pyridyl)siloxane tetramers

In response to the lack of success that had been encountered in synthesizing polymethyl(3-pyridyl)siloxanes, an entirely different approach was considered: a homogeneously-catalyzed synthesis of 3-triethylsilylpyridine (Figure 61),\textsuperscript{22} which was already under consideration for the synthesis of silylated pyridines (Section 3.6.5), was adopted for a tetramer synthesis with polyhydromethylsilane (M\textsubscript{n}: 390 g/mol) (Figure 62). The advantage of the proposed procedure was that the synthesis of a pure monomer could be avoided entirely.

![Figure 61 Synthesis of 3-triethylsilylpyridine](image-url)

Figure 61 Synthesis of 3-triethylsilylpyridine.\textsuperscript{22}
The original procedure was adapted to include procedural aspects of a similar reaction by Masuda et al.,\textsuperscript{23} which included running the reaction at 80 °C for several hours instead of at room temperature for several days. The reaction mixture was also cooled prior to the silane’s addition to prevent any unwanted side-reactions or decomposition. The first synthesis involved polyhydromethylsilane and 3-iodopyridine, with 5 mol % Rh catalyst and potassium phosphate (buffer) in 4 mL N-methylpyrrolidinone (NMP). A distribution of oligomers made up the polyhydromethylsilane reagent, given a $M_n$ of 390 g/mol. The oligomer most closely corresponding to this averaged mass was that of the tetramer at 402 g/mol, and so the ratio of silane to 3-iodopyridine was set at 1:4, and the amount of all other reagents were calculated relative to the 3-iodopyridine. The pyridine, catalyst and phosphate salt were dissolved together in the solvent and cooled to 0 °C, after which the silane was added dropwise; immediately following addition, the temperature was raised to 80 °C and the
reaction was left stirring for 4 h under a dynamic flow of Ar with a reflux condenser. The reaction was quenched with deionized water. To isolate the product oligomer, the solvent was removed under vacuum with heat, the product was dissolved in a mixture of hexane and dichloromethane, and filtered through a silica or Celite™ plug to remove the homogenous catalyst. The remaining solvent was removed under vacuum. The isolated, viscous liquid was analyzed with $^1$H NMR spectroscopy, and compared to reference $^1$H NMR spectra of the starting materials: a complete lack of the expected product’s Si-CH$_3$ proton signals proved the reaction had not been successful. The Si-H proton signals of the starting material were not observed either. It was considered that the polyhydromethylsilane, with a boiling point of approximately 177 °C, was being lost due to evaporation. Given that the reaction was run under a dynamic flow of Ar, and less than 0.5 mL of silane was added, it was not unreasonable to assume that, at 80 °C, the polyhydromethylsilane was slowly evaporating, condensing, and then remaining on the condenser. The procedure was subsequently modified.

The reaction was set up in the glovebox, following the same procedure as the previous synthesis, and run in a pressure tube to prevent any loss of starting material. To give the reaction the best chance at success, the reaction time was extended to days as opposed to hours: for the first 24 hours, the reaction mixture was left stirring in the glove box, which operates above ambient temperatures; afterwards, the reaction was relocated to a fumehood where it was heated to 65 °C for 48 hours. In keeping with the original procedure,$^{22}$ the reaction was allowed to stir at room temperature for four days. To test the success of the reaction, the crude reaction mixture was analyzed by NMR spectroscopy ($^1$H, COSY, HSQC), prior to any work up. The analysis suggested the
reaction had produced a pyridyl functionalized tetramer: the expected aromatic and Si-CH\textsubscript{3} signals were observed, with no evidence of the Si-H proton signals from the starting material. There were interfering signals in the NMR spectra, however, and analysis of the \textsuperscript{1}H and COSY spectra suggested that pyridine was a byproduct.

In order to fully characterize the product, and confirm the reaction’s success, the product oligomer needed to be isolated from the reaction mixture. The product mixture was vacuum distilled over three days and increasingly higher temperatures (≤ 180 °C). Subsequent \textsuperscript{1}H NMR analysis of the product mixture showed that the solvent, \textit{N}-(methylpyrrolidone, persisted in the isolated sample. This issue of removing NMP from polymers has been documented in the literature: in 2001, Ponzio et al.\textsuperscript{32} found that NMP could not be removed from free-standing polyaniline films by dynamic vacuum alone. They determined that NMP was hydrogen bonding to the aniline moiety of the polymer, and surmised that protonating the polymer would break the hydrogen bond network, allowing the NMP to be washed away with deionized water. It took more than four protonation/deprotonation cycles to completely remove NMP from the polymer films. Unfortunately, strong acid/base treatments of siloxanes could initiate depolymerization,\textsuperscript{33} and thus this procedure could not be followed.

Small-scale water extractions were attempted in place of vacuum distillation, the rationale being that the water-soluble reaction components (potassium phosphate and NMP) would dissolve into the aqueous layer, leaving the polymer and catalyst in the organic layer. Once isolated from the aqueous layer, the organic layer could be passed through a short basic alumina column to remove the catalyst and isolate the product oligomer.
For the test extraction, 0.2-0.3 mL of the reaction mixture was dissolved in 2 mL of deionized water and shaken vigorously. Due to the comparable densities of the reaction mixture and the water, it took over 36 hours to separate. Once isolated and filtered through a short basic alumina column, the organic layer was analyzed by $^1$H NMR spectroscopy; NMP persisted in the sample. Recognizing that NMP would not interfere with mass spectrometry, which would help to further characterize the product, it was decided to remove all catalyst and phosphate salt from the product mixture in order to continue analysis of the polymer. Another extraction was completed with 0.3 mL of the reaction mixture and 2 mL of water. After separating over 48 hours, the organic layer was isolated, dried over sodium sulfate, and filtered through a short basic alumina column, which was thoroughly washed with deuterated chloroform to ensure all organics were collected. The isolated organic layer was analyzed by $^1$H and $^{31}$P NMR spectroscopy; it was confirmed that the tetramer had been isolated phosphine free, and so the sample was submitted for mass spectrometry analysis.

The extracted product mixture was analyzed using EI-MS. The molar mass of the expected polymethyl(3-pyridyl)siloxane was 711 g/mol, however, a molecular ion peak was not observed. The most intense peak observed in the mass spectrum was at 520 m/z, a mass larger than either of the starting materials (3-iodopyridine: 204 g/mol; polyhydromethylsilane: ~390 g/mol). Any proposed fragmented structures had to be functionalized by at least three pyridyl rings to correspond to 520 m/z (Figure 63). While the results of the MS analysis were promising, the inability to isolate and fully characterize a purified tetramer made it impossible to move on to the next step in
establishing the project’s validity: reversibly hydrogenating polymethyl(3-pyridyl)siloxanes.

![Diagram of molecular structures]

**Figure 63** Proposed EI-MS fragments of the polymethyl(3-pyridyl)siloxane tetramer (m/z = 520).

It was recognized that, given the distribution of oligomers inherent in the polyhydromethylsilane reagent, the supply of 3-iodopyridine in the system could be exhausted before the synthesis of a fully pyridyl-functionalized siloxane was achieved. In order to move forward with this synthesis, the polyhydromethylsilane would have to be more fully characterized, and an oligomer with a specific number of repeat units would have to be isolated (possibly by gel permeation chromatography). The solvent, NMP, would have also had to be exchanged for a more volatile solvent, which could require an entire procedural re-optimization. The exceptionally long reaction time would also have to be addressed to increase the reaction’s efficiency. Given the number of issues that needed to be resolved before the synthesis could potentially succeed, it was decided to take a step back from this approach to polymethyl(3-pyridyl) siloxanes as hydrogen-storing liquids.
3.6.4 The third approach: synthesis and hydrogenation of 3-trimethylsilylpyridine

It was realized that the synthesis of polymethyl(3-pyridyl)siloxanes was not a trivial undertaking. To better understand why, the expertise of Dr. Michael Brook of McMaster’s University, author of *Silicon in Organic, Organometallic, and Polymer Chemistry* (2000), was sought. Dr. Brook expressed concern that the pyridyl rings of the proposed polymethyl(3-pyridyl)siloxanes may be basic enough to cause their depolymerization. He suggested focusing on the synthesis of more thermodynamically favoured cyclic oligomers to prevent the possibility of said depolymerisation. The synthesis of cyclic polymethyl(3-pyridyl)siloxanes trimers had already been attempted, however, and failed. There was a procedure outlined in the literature for the synthesis of a cyclic polychloromethylsiloxane tetramer, which could be incorporated into the synthesis of a cyclic polymethyl(3-pyridyl)siloxane tetramer (Figure 64); however, unless there was some indication a silylated pyridine ring could readily and reversibly dehydrogenate, the undertaking would be not worthwhile.

![Figure 64 Proposed synthesis of cyclic polymethyl(3-pyridyl)siloxane tetramers.](image-url)
As such, it was decided to synthesize 3-trimethylsilylpyridine (Figure 65). Although 3-trimethylsilylpyridine is not as representative of the proposed hydrogen storing polymethyl(3-pyridyl)siloxanes as the aforementioned species (Sections 3.6.1-3.6.3), a successful hydrogenation and dehydrogenation of 3-trimethylsilylpyridine would suggest that the presence of the silyl group does not impede these reactions. From this, it could be extrapolated that the reversible hydrogenation of larger polymethyl(3-pyridyl)siloxanes could be possible.

![3-trimethylsilylpyridine](image)

**Figure 65** 3-trimethylsilylpyridine.

3-Trimethylsilylpyridine was synthesized via a Grignard reaction (Figure 66). NMR and MS analysis confirmed that the synthesis was successful, with no observable side-products. To ensure purity, however, the compound was vacuum distilled. Once the pure compound was isolated, the conditions necessary for hydrogenation were explored (Table 26). The catalysts Pd/C and Rh/C were chosen due to their established use as pyridine hydrogenation catalysts. The H$_2$ pressure (70 bar) and initial reaction temperature (100 °C) were based upon reaction conditions optimized for the hydrogenation of substituted pyridines, as reported by Jessop et al. (Section 3.2.3).

![Synthesis of 3-trimethylsilylpyridine](image)

**Figure 66** Synthesis of 3-trimethylsilylpyridine.
The first hydrogenation trial of 3-trimethylsilylpyridine, performed at 100 °C, resulted in 0% selectivity for the hydrogenated product due to ring opening and/or decomposition of the starting material. The product(s) structure was not elucidated. The second trial was run at 50 °C to increase the reaction’s selectivity. The result was quantitative conversion after 24 hours with 100% selectivity for the desired 3-trimethylpiperidine, as confirmed by NMR analysis. The third trial was performed under the same conditions as the second, but at a lower catalyst loading; this was done to establish whether the same conversion could be achieved with less catalyst, as unnecessary resource depletion was to be avoided where possible. Unfortunately, the conversion dropped to 68% after 24 hours, and so the higher catalyst loading was maintained. While Rh/C did catalyze the desired reaction pathway to 3-trimethylpiperidine with 100% selectivity, it did so at a slightly slower rate than Pd/C (94% conversion versus 100%, respectively). It was concluded, however, that both catalysts were viable for the hydrogenation of silylated pyridines: both catalysts offered high selectivity with rates (i.e. reaction times) comparable to those reported by Jessop et al. Thus it was demonstrated that the presence of a silyl functionality does not inhibit

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**Table 26** Conditions and results from the hydrogenation of 3-trimethylsilylpyridine.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Catalyst</th>
<th>Loading (wt%)</th>
<th>H₂ Pressure (bar)</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd/C</td>
<td>5</td>
<td>70</td>
<td>100</td>
<td>21</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Pd/C</td>
<td>5</td>
<td>70</td>
<td>50</td>
<td>24</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Pd/C</td>
<td>1</td>
<td>70</td>
<td>50</td>
<td>24</td>
<td>68</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Rh/C</td>
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<td>50</td>
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<td>Rh/C</td>
<td>5</td>
<td>70</td>
<td>50</td>
<td>36</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
hydrogenation at sufficiently low temperatures, but may hasten degradation/ring opening at high temperatures. It is also interesting to note that there appeared to be no significant catalyst deactivation, as is often expected for systems containing metal-coordinating species such as pyridyl rings.\textsuperscript{36,37} Overall, this lent credence to the possibility that polymethyl(3-pyridyl)siloxanes could be rapidly, selectively and reversibly hydrogenated.

Having established the hydrogenation conditions of 3-trimethylsilylpyridine, the focus shifted to determining the dehydrogenation conditions. This aspect of the project was done in collaboration with Dominique Vanier, an honours student of the Jessop group.\textsuperscript{38}

### 3.6.5 The third approach continued: synthesis and reversible hydrogenation of silylated pyridines

The bulk synthesis and hydrogenation of 3-trimethylsilylpyridine was attempted so that there would be enough starting material to screen for the optimal dehydrogenation conditions of 3-trimethylsilylpiperidine. Unfortunately, repeating the previously outlined procedure for the synthesis of 3-trimethylsilylpyridine (Figure 66) was not successful. It was readily acknowledged that this failure was caused by the infiltration of water into the system from an overly humid laboratory environment. As such, a new synthesis was adopted from the literature: the procedure outlined by Yamanoi et al.\textsuperscript{22} detailing the synthesis of 3-triethylsilylpyridine, as discussed in Section 3.6.3 (Figure 67). Though there are structural differences between 3-trimethylsilylpyridine and 3-triethylsilylpyridine, those differences were not considered significant enough to affect
the hydrogenation/dehydrogenation results and their applicability to the more complex polymethyl(3-pyridyl)siloxanes.

Figure 67 Synthesis of 3-triethylsilylspyrindine, as described in Section 3.6.3.

Three separate syntheses were attempted based on the outlined procedure. It was unclear whether the reactions had been successful due to the existence of multiple aromatic species observed in the \(^1\)H NMR spectrum (e.g. product, starting material). Isolation and purification of the desired product was hindered, unfortunately, due to a lack of detail in the literature procedure. While column chromatography was cited as the method of purification, details of the solvent system used were absent. Yamanoi et al. did outline their chromatographic procedure for the isolation of a trialkylsilyl-containing synthetic retinoid benzoic acid derivative (TAC), however, with a solvent system containing hexanes and ethyl acetate. Using that information, the determination of a suitable solvent system was attempted using silica and alumina thin layer chromatography (TLC). Solvent systems tested included chloroform, hexanes and ethyl acetate, as well as 1:1, 2:3, 1:2, and 3:1 mixtures of ethyl acetate and hexanes. Unfortunately, none of the solvent systems tested provided adequate separation between the components of the reaction mixture to allow for isolation and elucidation. Subsequently, this synthesis was abandoned.
Given the unexpected difficulties encountered in the synthesis of silyl-functionalized pyridines, the focus shifted to determining the hydrogenation/dehydrogenation conditions of 2-trimethylsilylpyridine (Figure 68). 2-Trimethylsilylpyridine became of interest for two reasons: it was commercially available, and it was expected that its ortho substituent would help increase its rate of dehydrogenation. This expectation stemmed from reports published by Dean et al. that suggested dehydrogenation rates of ortho substituted N-heterocycles (i.e. 2,6-di-tert-butylpyridine) are markedly faster than the corresponding unsubstituted N-heterocycles. Dean et al. rationalized that the bulky ortho substituent(s) prevented the ring nitrogen from coordinating to the heterogeneous catalyst, inhibiting catalyst poisoning by the substrate and allowing the dehydrogenation to occur at higher rates. Subsequently, it was theorized that choosing an ortho substituted silyl pyridine as a new representative polymethylpyridylsiloxane analogue may give the system its best chance of success; and that, if 2-trimethylsilylpyridine could be readily and reversibly hydrogenated, it would support the validity of the overall project. It would also suggest that a N-C-Si bond would be resistant to hydrolytically and/or hydrogenolytically cleaving, a concern that originally lead to the synthesis of 3-pyridyl analogues, thus allowing polymethyl(2-pyridyl)siloxanes to also be considered for use as hydrogen-storing liquids.

![General hydrogenation / dehydrogenation of 2-trimethylsilylpyridine.](#)
2-Trimethylsilylpyridine was successfully hydrogenated to 2-trimethylsilylpiperidine with 100% conversion and selectivity over 5 mol% Rh/C after 48 hours at 75 °C under 70 bar H₂. The rate of hydrogenation was slower than that of 3-trimethylsilylpyridine despite the higher reaction temperature: 48 hours versus 24 hours at 75 °C versus 50 °C, respectively. This was not unexpected, however. The first step in the heterogeneous catalyzed hydrogenation of pyridine involves the N-heterocycle binding to the metal surface via the nitrogen lone pair of electrons.39 The steric hindrance of the ortho-substituted trimethylsilylgroup would interfere with that binding mode, thus slowing the rate of hydrogenation. Having successfully obtained 2-trimethylsilylpiperidine, however, its dehydrogenation was attempted. The dehydrogenation conditions were based upon the procedure established by Dean et al. for the dehydrogenation of ortho substituted pyridines:37 Rh/C (1 mol% loading) under a dynamic flow of Ar at 150 °C. The reaction temperature was set at 150 °C because the boiling point of both the starting material and product was approximately 180 °C. The reaction was carried out over 20 hours in an attempt to ensure complete conversion.

Despite best efforts, however, no conversion to 2-trimethylsilylpyridine was observed. This was not expected: under similar conditions (170 °C, 1 mol% Pd/SiO₂, 1 h) Dean et al.37 observed a 40% conversion to 2,6-di-tert-butylpyridine from 2,6-di-tert-butylpiperidine. Despite the structural difference between 2,6-di-tert-butylpiperidine and 2-trimethylsilylpiperidine, and fact that the dehydrogenation of 2-trimethylsilylpiperidine was run at a lower temperature (150 °C), the differences between the systems are not so great that a 0% conversion is reasonable after 20 hours. While it is possible that some product was lost due to evaporation given the length of reaction time, it seems unlikely
that it would have been lost completely, given that the piperidine and pyridine have similar boiling points and similar attractive intermolecular forces (e.g. hydrogen bonding). This result suggested that the silyl group does inhibit the dehydrogenation process.

The cause for this observed inhibition was not further investigated, however the general mechanism of piperidine/pyridine dehydrogenation/hydrogenation may suggest an explanation. In both mechanisms, the N-heterocycle interacts with the catalytic surface via the nitrogen lone pair. In their investigation of the analogous 2-methylquinoline, Mochida et al. suggested that the hydrogenation of 2-methylquinoline may be favored, in part, due to the release of steric strain around the N-metal binding site. They postulated that the transition from planarity to non-planarity would result in a favorable reduction in steric interactions at the N-metal binding site, thus favoring the hydrogenation reaction despite the presence of the ortho substituent. This would suggest, however, that the dehydrogenation of 2-methylquinoline would not be highly favored due to the subsequent increase in steric interactions. It is possible, therefore, that the hydrogenation of 2-trimethylsilylpyridine was favored due to this reduction in steric interactions, and that the dehydrogenation was not favored due to the inherent increase in steric interactions. While this is contrary to the results observed by Dean et al., it would suggest that catalytic poisoning by the N-heterocycle is less important than sterics for this particular system.

The results of this investigation did not bode well for the viability of the overall project: the use of polymethylpyridylsiloxanes as hydrogen-storing liquids. The results suggested that a silyl-functionalized piperidine may not readily dehydrogenate, which
would render the overall project nonviable. It was recognized, however, that the position of the silyl group may be the problem, not the functional group itself. Consequently, one last attempt was made to synthesize, hydrogenate and dehydrogenate a polymethyl(3-pyridyl)siloxane (or an analogue thereof) in order to determine the project’s viability.

### 3.6.6 The final approach: synthesis and hydrogenation of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane

In a final attempt to determine whether polymethylpyridylsiloxanes could viably be used as hydrogen-storing liquids, the synthesis of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane was proposed (Figure 69). It was recognized that this bis(3-pyridyl)siloxane was a fairly accurate representation of the polymethyl(3-pyridyl)siloxanes in question, and that its synthesis could be designed to avoid some of the synthetic pitfalls experienced previously (Section 3.6.1-3.6.3), as well as the potentially problematic ortho substitution (Section 3.6.5). The synthesis of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane had been previously documented in the literature as part of the synthesis and characterization of pyridinyldisiloxanes and macrometallacyclic materials. It involved a lithium halogen exchange between n-butyllithium and 3-bromopyridine, which was then quenched with 1,3-dichloro-1,1,3,3-tetramethylsiloxane to form the bis(3-pyridyl)siloxane (Figure 70). The product was successfully synthesized, as confirmed by NMR and HR-MS analysis. Isolating and purifying the bis(3-pyridyl)siloxane, however, proved yet again to be problematic. $^1$H NMR analysis revealed the presence of alkyl-based impurities, of which only some of the $^1$H NMR peaks corresponded to the expected by-product bromobutane. There was also an
intense signal at 0 ppm, which alluded to the presence of a methylsilyl species despite the fact that tetramethysilane (TMS) was not used as an NMR reference, and silicon grease was not used on the reaction glassware.

![Figure 69](image.png)

**Figure 69** 1,1,3,3-Tetramethyl-1,3-(3-pyridyl)siloxane.

![Figure 70](image.png)

**Figure 70** Synthesis of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane.

The literature procedures detailed purification techniques involving either vacuum distillation or column chromatography. Separation by column chromatography, however, failed to isolate the product from the observed impurities. Vacuum distillation was successful in removing essentially all bromobutane from the reaction mixture; however, the unidentified alkyl impurity persisted, as did the unidentified impurity responsible for the intense signal at 0 ppm. HMBC (29Si) analysis of the product mixture showed two Si-H correlated signals: one at -0.54 ppm, correlating to the pyridine ring hydrogens, and one at -19.9 ppm, correlating to the hydrogen signal at 0 ppm. It was considered that this impurity may have resulted from the infiltration of water into the system, causing the 1,3-dichloro-1,1,3,3-tetramethysiloxane starting material to hydrolyze. Comparing the 29Si peak at -19.9 ppm with 29Si NMR correlation charts
suggested that the anomalous peak could be representative of a cyclic polymethylsiloxy species such as octamethylcyclotetrasiloxane, which is known to predominate in similar hydrolysis reactions. A cyclic species seemed most likely because there were no additional Si-H peaks that may have suggested an end-group. Given the persistent complications encountered in the synthesis of methylpyridylsiloxanes, it was decided to proceed with the hydrogenation of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane despite the persisting impurities; the expectation was that the said impurities would not affect the hydrogenation reaction.

The hydrogenation conditions of the bis(3-pyridyl)siloxane (Table 27) were initially mirrored after the previously discussed hydrogenation conditions of 3-trimethylsilylpyridine (Section 3.6.4). The expectation was that 100% conversion and selectivity would be observed; unfortunately the % conversion was zero (Trial 1). For the second trial, the temperature was increased to 95 °C, which was intentionally set below the 100 °C ceiling established during the hydrogenation trials of 3-trimethylsilylpyridine. Unfortunately, degradation/proliferation of side products still occurred, as evidenced by anomalous signals and integrations in the $^1$H NMR analysis. The structures of these products were not elucidated. For the third trial, the conditions for the hydrogenation of 2-trimethylsilylpyridine were adopted (Section 3.6.5): after 48 hours at 75 °C, however, the conversion was still less than 100%. For the fourth and final trial, the temperature was increased slightly and the reaction time increased to 96 hours in order to obtain 100% conversion. The results of trials 1 and 3, the conditions of which provided 100% conversion and selectivity for the analogues 3- and 2-trimethylsilylpyridine respectively, suggested that an increase in chain length may result in a significant increase in reaction
time. Such an increase could require a significant increase in catalyst loading in order to compensate, thus contributing to resource depletion and potentially prohibitive operation costs.

Table 27 Conditions and results of the hydrogenation of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Catalyst</th>
<th>Loading (mol %)</th>
<th>H₂ Pressure (bar)</th>
<th>Temp (°C)</th>
<th>Time (hours)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh/C</td>
<td>5</td>
<td>70</td>
<td>50</td>
<td>24</td>
<td>0</td>
</tr>
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<td>70</td>
<td>95</td>
<td>36</td>
<td>78</td>
</tr>
<tr>
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<td>Pd/C</td>
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<td>70</td>
<td>75</td>
<td>48</td>
<td>79</td>
</tr>
<tr>
<td>4</td>
<td>Pd/C</td>
<td>5</td>
<td>70</td>
<td>80</td>
<td>96</td>
<td>100</td>
</tr>
</tbody>
</table>

The product isolated from the third and fourth trials was fully, and separately, analyzed by MS and NMR spectroscopy in order to determine selectivity. There were anomalies in the analysis of the expected 1,1,3,3-tetramethyl-1,3-(3-piperidyl)siloxane product, however: the integration of the ¹H NMR signal at 0.05 ppm, corresponding to the SiCH₃ peaks, integrated to twice the expected number of hydrogens; and the HR ESI-MS analysis showed a Gaussian-like mass distribution from 301 m/z to 745 m/z with a mass separation of 74 m/z (Figure 71). HMBC (²⁹Si) analysis of the expected 1,1,3,3-tetramethyl-1,3-(3-piperidyl)siloxane showed two distinct Si peaks: one peak at 6.4 ppm that correlated to the piperidine ring hydrogens, and one peak at -21.2 ppm that correlated to the hydrogen signal at 0.05 ppm. Comparing the ²⁹Si peak at -21.2 ppm with ²⁹Si NMR correlation charts suggested that the anomalous peak likely corresponded to a polymethylsiloxyl species. This was corroborated by the HR ESI-MS data: the mass separation of 74 m/z is equal to the mass of the repeat unit, [Si(CH₃)₂O]ₙ.
Taking the results of this analysis under consideration, it was proposed that the cyclic polymethylsiloxyl impurity observed in the synthesis of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane did in fact affect the hydrogenation reaction: the cyclic polymethylsiloxyl species may have undergone Si-O bond cleavage on the catalyst’s surface, and reacted with the bis(pyridyl/piperidyl)siloxane to give a distribution of piperidyl-terminated dimethylsiloxanes of increasing chain length. This was corroborated by the HR ESI-MS results. The mass distribution evident in the ESI-MS spectrum began at a mass to charge ratio of 375.23, which corresponds to the exact mass of protonated 1,1,3,3,5,5-hexamethyl-1,5-(3-piperidyl)siloxane (Compound 1, Table 28), as confirmed by mass spectrum predicting software. ESI-MS employs a softer ionization technique, and thus is conducive to protonated, not fragmented, species. It was found that each peak of the mass distribution observed in the ESI-MS spectrum correlated to the mass of a piperidyl-terminated dimethylsiloxane, each with a sequentially longer chain length (Table 28).
Table 28 HR ESI-MS analysis of the proposed piperidyl terminated dimethyl siloxanes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Proposed Structure</th>
<th>Observed m/z&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Calculated m/z&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
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<tr>
<td>1</td>
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<td>375.232</td>
<td>375.232</td>
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<tr>
<td>2</td>
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</tr>
<tr>
<td>6</td>
<td></td>
<td>745.327</td>
<td>745.325</td>
</tr>
</tbody>
</table>

<sup>a</sup> Mass of protonated proposed structure; <sup>b</sup> Calculated by mass spectrum predicting software
The mechanism by which these piperidyl-terminated dimethylsiloxanes could be formed is, as of yet, unknown. There is precedence in the literature for Si-O bond cleavage on heterogeneous catalysts: studies have found that polydimethylsiloxane degrades into dimethylsilanediol (HO-Si(CH3)2-OH) over dry clays.44,45 There is also precedence for the synthesis of similarly functionalized dimethylsiloxanes: in 1992, Nagase et al. synthesized oligodimethylsiloxanes terminated at one end with a 2-(4-pyridyl) ethyl group (Figure 72).42 As such, it is possible that pyridyl-terminated dimethylsiloxanes were formed first, followed by hydrogenation of the pyridyl ring to give piperidyl-terminated dimethylsiloxanes.

![Figure 72 Example of a prepared pyridyl-terminated reactive oligodimethylsiloxane.](image)

The second step in pyridine’s hydrogenation mechanism involves the ring laying parallel to the catalyst surface;39 this suggests that the bis(pyridyl)siloxane would also be held parallel to the catalyst surface during hydrogenation, a favorable position for Si-O bond cleave to occur. Taking this information into consideration, a mechanism was proposed where the cyclic dimethyl- siloxane and bis(3-pyridyl)siloxane undergo Si-O bond cleavage, migration, and reaction on the catalyst’s surface to form pyridyl-terminated dimethylsiloxanes. These pyridyl-terminated dimethylsiloxanes then hydrogenate to give the observed piperidyl terminated dimethylsiloxanes (Figure 73). It is important to note that, while the elements of this proposed mechanism are supported by
the literature (*vide supra*), it was not within the scope of the project to undertake a complete mechanistic study in order to support or refute it.

![Proposed mechanism for the formation of piperidyl-terminated dimethylsiloxanes](image)

**Figure 73** Proposed mechanism for the formation of piperidyl-terminated dimethylsiloxanes, wherein (*) indicates coordination to the heterogeneous catalyst’s surface.

The results of the hydrogenation of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane were entirely unexpected. While it was evident that the pyridine ring did successfully hydrogenate, the formation of piperidyl-terminated dimethylsiloxanes in place of 1,1,3,3-tetramethyl-1,3-(3-piperidyl)siloxane suggests that any produced or preexisting siloxyl species in the reaction mixture will complicate or inhibit the hydrogenation of polymethyl(3-pyridyl)siloxanes. Such an extreme sensitivity to the presence of impurities would make hydrogenating polymethylpyridylsiloxanes on an industrial scale quite challenging. As the desired 1,1,3,3-tetramethyl-1,3-(3-piperidyl)siloxane was not isolated from the hydrogenation of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane, it was not possible
to establish the conditions of, or even attempt, the dehydrogenation reaction to show that polymethylpyridylsiloxanes could be reversibly hydrogenated. Subsequently, it was concluded that implementing polymethylpyridylsiloxanes as hydrogen-storing liquids was not viable.

### 3.7 Conclusion

We had originally proposed using polymethylpyridylsiloxanes as hydrogen-storing liquids in response to the Hydrogen Initiative (Section 1.3). It was expected that establishing the validity of such a proposed project would be relatively facile: synthesize a polymethyl(3-pyridyl)siloxane, then hydrogenate and dehydrogenate it. Once the project was shown to be viable, the optimization of the chemistry and engineering could then commence to implement polymethylpyridylsiloxanes as hydrogen-storing liquids. Unfortunately, a polymethylpyridylsiloxane was not successful synthesized and reversibly hydrogenated, and consequently, the project had to be deemed not viable.

It is true that there is precedence in the literature for the synthesis of polymethylpyridylsiloxanes, as well as for the hydrogenation of N-heterocyclic functionalized polymers. Under no circumstances are we claiming that the chemistry is not possible, only that the challenges presented by the chemistry are enough to render the project impractical. Nearly every attempted synthesis of a polymethylpyridylsiloxane, or analogue thereof, was mired with complication or failure (Section 3.6.1-3.6.5); and even if those complications could be overcome, there would still remain a very real possibility that the polymethylpyridylsiloxanes synthesized would be depolymerized by their own
pendant pyridyl rings.\textsuperscript{33} Even if those synthetic and stability issues could be compensated for, the challenges posed by the hydrogenation of polymethyl(3-pyridyl)siloxanes would remain (Section 3.6.6).

The results of the hydrogenation of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane suggest that, under hydrogenation conditions, any siloxyl-based impurity could react with the desired polymethyl(3-piperidyl)siloxanes, rendering them nonviable as hydrogen-storing liquids. While this problem might be solved by a rigorous synthetic and purification procedure, just the potential for such a degradation reaction to occur poses a significant threat to the industrial applicability of polymethylpyridylsiloxanes. The costs associated with losing an entire lot of polymethyl(3-piperidyl)siloxanes due to product degradation could be prohibitive on an industrial scale.

In the end, however, even if all of the challenges exposed in this investigation were overcome, even if the polymethylpyridylsiloxanes were synthesized and their hydrogenation/dehydrogenation conditions optimized, the resulting hydrogen-storing liquids would not meet the DoE’s requirements for H\textsubscript{2} based technologies. The proposed siloxanes themselves only offer a 4.2 wt% H\textsubscript{2} storing capacity; the DoE’s 2017 targets require a 5.5 wt% capacity for the \textit{entire system} (e.g. the hydrogen-storing liquid, plus all associated machinery).\textsuperscript{46}

As such, it was concluded, based on the synthetic challenges encountered, and the industrial consequences of those challenges, that implementing polymethyl(3-pyridyl)siloxanes as hydrogen-storing liquids is not viable.
3.8 References


(41) Uhlig, F.; Marsmann, H. 29Si NMR Some Practical Aspects.


3.9 Appendix: NMR spectra of select compounds

Figure 74 $^1$H NMR of 3-trimethylsilylpyridine

The NMR spectrum shows the chemical shifts and intensities of the protons in the 3-trimethylsilylpyridine molecule. The chemical shifts are marked with blue and red peaks, indicating the proton positions and their intensities.
Figure 75 $^1$H NMR of 3-trimethylsilylpiperidine.
Figure 76 COSY of 3-trimethylsilylpiperidine.
**Figure 77** HSQC of 3-trimethylsilylpiperidine.
Figure 78 $^1$H NMR of 1,1,3,3-tetramethyl-1,3-(3-pyridyl) siloxane.
Figure 79 $^{29}$Si HSQC of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane.
Figure 80 $^1$H NMR of 1,1,3,3-tetramethyl-1,3-(3-piperidyl)siloxane mixture (See Section 3.6.6).
Figure 81 COSY of 1,1,3,3-tetramethyl-1,3-(3-piperidyl)siloxane mixture (See Section 3.6.6).
**Figure 82** HSQC of 1,1,3,3-tetramethyl-1,3-(3-piperidyl)siloxane mixture (See Section 3.6.6).
Figure 83 $^{29}$Si HSQC of 1,1,3,3-tetramethyl-1,3-(3-piperidyl)siloxane mixture (See Section 3.6.6).
Chapter 4

Conclusions and Considerations

4.1 Polymethylpyridylsiloxanes

Polymethylpyridylsiloxanes had originally been proposed for use as hydrogen-storing liquids for vehicular applications. Despite the expectation that it would be relatively straightforward to validate and implement such a proposed project, the polymethylpyridylsiloxanes were not successfully synthesized and reversibly hydrogenated, and consequently, the project was deemed non-viable (see Chapter 3). Every attempted synthesis of a polymethylpyridylsiloxane, or analogue thereof, was mired with complication or failure: either the desired product was not synthesized, or it could not be isolated from the reaction mixture or side-products. Even if these synthetic complications could have been overcome, there is precedence in the literature that suggests that the pendant pyridyl rings of the proposed polymethylpyridylsiloxanes could have catalyzed the siloxanes’ own depolymerization.¹ Such stability issues would have made implementing polymethylpyridylsiloxanes as industrial and/or commercial energy carriers impossible; their operational lifetimes would simply have been too short to be economical. Industrial and/or commercial implementation would have been further complicated by the challenges posed when hydrogenating polymethylpyridylsiloxanes. The attempted hydrogenation of 1,1,3,3-tetramethyl-1,3-(3-pyridyl)siloxane suggested that any siloxyl-based impurities present could react with the polymethylpyridylsiloxanes, rendering them nonviable as hydrogen-storing liquids. The
costs associated with such product degradation would be prohibitive if it were to occur on an industrial scale.

Additionally, the hydrogen-storing capacity of the proposed polymethylpyridylsiloxanes was below the DoE’s requirements for H$_2$ based technologies. The siloxanes themselves would have only offered a 4.2 wt% H$_2$ storing capacity; the DoE requires a 4.5 - 5.5 wt% capacity for the *entire system* (e.g. the hydrogen-storing liquid, plus all associated on-board equipment). While the lower hydrogen-storing capacity of the proposed polymethylpyridylsiloxanes had been known from the beginning of the project, it was expected that continuing research would eventually produce a hydrogen-storing system that met all of the DoE’s requirements. Looking forward, however, the implementation of such hydrogen-storing siloxanes, or any hydrogen-storing liquid, as alternative energy carriers to fossil fuels would require retrofitting existing vehicular and refueling infrastructures in order to be successful. Vehicles would have to be outfitted with equipment optimized for on-demand H$_2$ evolution from the siloxanes, and with a fuel cell system optimized to convert that evolved H$_2$ into the electricity necessary to power the vehicle. The current refueling infrastructure would have to be modified to accommodate a liquid energy carrier with different properties (e.g. viscosity, density, etc.) than that of fossil fuels, and to permit the dehydrogenated liquid to be collected from vehicles, and stored, until transported to a factory for re-hydrogenation. Additionally, current factories would have to be retrofitted, or new factories would have to be built, to specialize in re-hydrogenating the hydrogen-storing siloxanes.
Overall, the development and optimization necessary to shift from fossil fuels to hydrogen-storing siloxanes as energy carriers would not be insignificant; this would have likely inhibited the siloxanes’ use in vehicular applications, even if their synthesis and reversible hydrogenation had been successful, and their hydrogen-storing capacities had been higher. This fact has been exemplified by other vehicular hydrogen-based technologies, such as the H₂ internal combustion engine (Chapter 1, Section 1.6.2). A H₂ internal combustion engine (ICE) offers better fuel efficiency than conventional ICES and produces nearly no carbonaceous or noxious emissions. Despite these advantages, and the relative ease of modifying conventional ICES to burn H₂, H₂ ICES have not been implemented on a larger scale due to a lack of H₂ refueling infrastructure.

Subsequently, after taking into consideration the synthetic challenges that have been faced, and the complications that would arise during large-scale implementation, it has been confidently concluded that the use of polymethylpyridylsiloxanes as hydrogen-storing liquids for vehicular applications is not viable.

4.2 Thermally Regenerative Fuel Cell System

Our thermally regenerative fuel cell (TRFC) system was proposed to supplement or supplant a vehicle’s alternator by converting wasted heat energy from the internal combustion system (i.e. engine, catalytic converter, exhaust, etc.) into electricity. It was proposed that this electricity could be used to charge a battery, or used directly to power auxiliary vehicular components such as lights, radio, or cooling/heating systems, etc. The objective of the project was to optimize the dehydrogenation reaction of the proposed TRFC system: to identify a heterogeneous catalyst that could provide a selectivity of 99.0
Pd/SiO$_2$ was chosen as the dehydrogenation catalyst due to its excellent selectivity (99.65%) and stability. The ideal selectivity of ≥ 99.9% was never realized however, and a concession had to be made that the desired selectivities of ≥ 99.9% for propiophenone were likely unattainable. It was recommended, therefore, that contingencies be engineered into the TRFC system to compensate for the catalyst’s inherent heterogeneity, and that a selectivity no higher than 99.0% should be assumed for the dehydrogenation reaction when calculating the expected operational lifetime of the working fluid.

The selectivity of the hydrogenation reaction was determined to be 98%, as described by Dr. Darrell Dean in his PhD dissertation. Consequently, one complete chemical cycle, wherein both the dehydrogenation and hydrogenation reactions are included, has an overall selectivity of 97%; the number of chemical cycles that could therefore occur before 50% of the working fluid is converted to unreactive side products, and needs to be replaced, is about 25 cycles (based on Section 2.4, Figure 26). While this number may seem low, it is important to note that the length of time between refueling is dependent not only on the number of cycles, but on the volume of liquid used. The flow rates required to achieve the necessary power output will also have a large impact on running time, and would likely be dynamic to compensate for the changing reaction rates and power demands.

During the early development of the TRFC system, Dr. Andrew Carrier determined that the initial dehydrogenation rate of 1-phenyl-1-propanol over Pd/SiO$_2$ at 200 °C is 22 mol H$_2$ per mol Pd per min over the first 10 min, or 0.21 mol H$_2$ per g Pd per min. If the TRFC’s proposed fuel cell stack could convert all of the H$_2$ evolved at
this rate into electricity with perfect efficiency, the stack could produce up to 665 A per g Pd in the dehydrogenation reactor. Using the hydrogenation reaction’s enthalpy and entropy values ($\Delta H^\circ = -56.3 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -119.1 \text{ J mol}^{-1} \text{ K}^{-1}$; see Section 2.2.1) to calculate the Gibbs free energy, a modest fuel cell voltage of 64 mV can be estimated. A voltage of 64 mV could provide upwards of 43 W of power per g Pd in the dehydrogenation chamber. Commercial trucking alternators however, which the TRFC system aims to supplant, operate at 12 V and 100-300 A, with a power output of 1200-3600 W. To increase the dehydrogenation rate to produce that much power, approximately 28 g of palladium would be required. If the re-hydrogenation at the cathodes of the fuel cell stack is assumed to operate at one fifth of that efficiency, another 140 g of Pd would be required. At nearly 170 g Pd per TRFC system, there is a very real concern that its implementation could significantly affect the global supply of Pd. The expectation, however, is that the development and optimization of the electrochemical reduction of propiophenone to 1-phenyl-1-propanol, and further, the development and optimization of a fully functioning TRFC system, will negate the need for such excessive amounts of Pd.

Additionally, Pd prices are currently greater than US $700 per oz. (or > US $25 per g); if the amount of required Pd stayed at 170 g, the Pd costs alone would be more than $4,200 for each TRFC system. This may seem prohibitive to its commercial implementation, but not if one considers the possible cost savings. Considering a maximum fuel savings of 10% (see Section 2.1.3), and the fuel expenditures of Canadian trucking companies in 2000, savings of 4,900 - 9,300 L fuel and $6,000-11,000 per truck
per year could be expected.\textsuperscript{5} Consequently, the up-front costs of implementing the TRFC system could be paid off within one year from fuel cost savings.

Furthermore, the TRFC system could contribute to significant decreases in anthropogenic CO\textsubscript{2} emissions. The Canadian trucking industry emits approximately 17 billion kg CO\textsubscript{2} per year;\textsuperscript{6} implementation of the TRFC system could reduce that amount by 340 million – 1.7 billion kg CO\textsubscript{2} per year. This could have a very real impact on atmospheric CO\textsubscript{2} levels, and would be a significant step in reducing the anthropogenic causes of climate change.

4.3 Extreme Selectivities

The inherent heterogeneity in heterogeneous catalysts can limit the ability to achieve reproducibly high selectivities for heterogeneous catalyzed reactions. When high selectivities have been reported in the literature for heterogeneous catalyzed reactions, the selectivities are often reported as being > 98, > 99, or 100 \%.\textsuperscript{7–9} Such literature reports make no attempt to establish whether > 99 \% or 100 \% selectivity is actually 99.9, or 99.99, or 99.999 \% selectivity, and whether or not those selectivities are truly reproducible to the second or third decimal place across multiple reactions. Thus, developing a method to reproducibly achieve selectivities of \(\geq 99.9\)% could provide researchers the ability to confidentially acquire reproducible, extreme selectivities.

Reproducible, extreme selectivities of \(\geq 99.9\)% were sought for the TRFC’s dehydrogenation reaction because a higher overall selectivity for each dehydrogenation-hydrogenation cycle would translate into longer operational lifetimes for the TRFC’s working fluid. The highest selectivity that could be achieved, however, was 99.65%, and
that was not readily reproducible across every reaction and every commercially available sample of Pd/SiO$_2$. There was simply too much heterogeneity in the commercial heterogeneous catalysts to afford that kind of extreme, reproducible selectivity. That being said, the quest for reproducibly extreme selectivities, via the careful selection of a catalytically active material’s size, shape and support material, is not one that should be abandoned. Not only would that kind of reproducible, extreme selectivity benefit systems such as our proposed thermally regenerative fuel cell, it could also benefit any industrial process that employs heterogeneous catalysts to increase production. Industrial processes are designed to be as resourceful and economical as possible: small increases in selectivity (0.5 - 2%) could raise profit margins; larger increases in selectivity ($\geq$ 99.9%) could result in millions, if not billions of dollars in increased product production, depending on the industrial process.

Consider, for example, the production of styrene. Styrene is one of the important aromatic monomers produced industrially. By 2004, nearly $6 \times 10^6$ metric tonnes of styrene was being produced annually in the US, primary for the production of polystyrene and other plastics. Styrene is produced by dehydrogenating ethylbenzene over an iron oxide-potassium oxide catalyst, at temperatures exceeding 500 °C. Ethylbenzene is produced via benzene alkylation with ethylene, in the presence of acidic catalysts. Ethylbenzene production is often complicated, however, by the formation of polyalkylated side-products, called polyethylbenzenes (PEB). To prevent PEB formation, the catalyst is varied, or the benzene to ethylene ratio is increased; however, to recover and recycle the unreacted benzene, equipment complexity and energy consumption must increase. Styrene production is also complicated by the formation of by-products such as
benzene and toluene, which account for yield losses upwards of 1% to 2%, respectively. If extremely selective heterogeneous catalysts could be developed for industrial processes such as the syntheses of ethylbenzene and styrene, production plant construction could be streamlined, operational costs could be minimized, production yields could be increased, handling and/or disposal of unwanted by-products could be eliminated, and profit margins could increase.\textsuperscript{10}

The fine chemicals industry could also benefit from the development of extremely selective heterogeneous catalysts. Many pharmaceuticals are first developed in milligram scales through complex, multi-step total syntheses, such as the total syntheses of prostaglandins. Making enough of a potential pharmaceutical for biological testing can be cost and labor intensive. If using an extremely selective catalyst in a total synthesis could increase the yield of even one reaction, such as the heterogeneous-catalyzed hydrogenolysis step of the Prostaglandin E2 Corey synthesis (Figure 84),\textsuperscript{11} the overall yield would increase. This could translate into significant time and cost savings while developing the burgeoning pharmaceutical, and could dramatically minimize the amount of waste produced by the process.

Consequently, while developing extremely selective heterogeneous catalysts would not be an easy undertaking, the long-term payoff may include industrial and/or pharmaceutical syntheses that produce less waste, consume less energy, and offer superior quality products than what has previously been possible.
4.4 Looking Forward

It takes time to develop systems such as our TRFC system. There are many components that require optimization: the dehydrogenation and hydrogenation reactions; the equipment necessary to retrofit TRFCs to vehicles; the fuel cell itself. It has taken six years, three PhD dissertations,\textsuperscript{3,4} and one Master’s thesis\textsuperscript{12} to get to the point where a prototype of the TRFC system may be possible. As we wait for such fuel-saving and environment-protecting technologies to develop, global fossil fuel supplies continue to dwindle and atmospheric CO\textsubscript{2} levels continue to rise. While it may be generations yet before the fossil fuel supply is completely depleted and climate change has irrevocably affected the planet, it will happen eventually. To help prevent the inevitable, it might be useful to develop interim technologies, which can be implemented now while more promising, long-term technologies and/or alternative energy carriers are being developed. One possible interim technology is the H\textsubscript{2} internal combustion engine (see Section 1.6.2).

Hydrogen internal combustion engines (ICEs) are an attractive interim technology because gasoline ICEs can be retrofitted to burn H\textsubscript{2}, often with very few complications. Neither a significant amount of time nor money would have to be invested to develop that
component of the technology. The production, transportation, and storage of H\textsubscript{2} already occurs on industrial and/or commercial scales; that aspect of the H\textsubscript{2} refueling infrastructure has already been developed, and would likely only require some optimization before H\textsubscript{2} ICEs could be effectively implemented. Additionally, H\textsubscript{2} ICEs can operate on lean fuel mixtures, where the amount of H\textsubscript{2} consumed is below the theoretical amount required for combustion. Since H\textsubscript{2} ICEs can run on sub-stoichiometric amounts of H\textsubscript{2}, the amount of fossil fuels that would have to be diverted to H\textsubscript{2} production could be minimized; and, by running H\textsubscript{2} ICEs on lean mixtures, the production of carbonaceous and/or noxious emissions will be practically non-existent. Subsequently, the implementation of H\textsubscript{2} ICEs could dramatically decrease anthropogenic sources of greenhouse gases.\textsuperscript{13}

The reason H\textsubscript{2} ICEs have not been widely adopted, and may not be suitable for long-term use, is in part due to the fact that the power output of H\textsubscript{2} ICEs is about 15\% less than that of gasoline ICEs, and thus would not be readily applicable to vehicles requiring higher energy outputs. Hydrogen ICE-powered vehicles are also less efficient than H\textsubscript{2} fuel cell-powered vehicles, which can travel farther per unit of H\textsubscript{2}. Additionally, there is a critical lack of public refueling infrastructures, and of technicians specifically trained to repair and maintain H\textsubscript{2} powered ICEs. There is also a lower on-board stowing capacity due to the H\textsubscript{2} storage tanks, which could be less appealing to some consumers. These issues are not insurmountable, however; and some could be solved simply by implementing H\textsubscript{2} / natural gas fuel blend ICEs instead of full H\textsubscript{2} ICEs. Overall, H\textsubscript{2} ICEs could be a suitable interim alternative to fossil fuel-powered systems, and most importantly, they could be implemented \textit{now}, not after 10 more years of development and
optimization. An interim technology such as H$_2$ ICEs could buy us the time to develop cleaner, more efficient systems to meet our energy demands, while simultaneously reducing fossil fuel consumption and greenhouse gas emissions.$^{13}$

### 4.5 Parting Words

The effect human beings have had on this planet cannot be undone overnight. We are polluting our land, our water, our atmosphere, and we are depleting Earth of its natural resources. Any attempt we make to undo this damage, however small (Chapter 2), is a step in the right direction. Even if one of our attempts fails (Chapter 3), we can still learn from the knowledge acquired while trying to develop and study it. Such work serves to move society forward, toward a reality where our world is not threatened by environmental collapse and energy crisis.

So, for the researchers out there who are trying to take that step in the right direction, don’t give up. For better or for worse, your work does matter and it will help move your field of research forward. Good luck.
4.6 References


(4) Carrier, A. J. The Transportation and Transformation of Energy Through Reversible Hydrogenation. PhD, Chemistry, Queen’s University, 2011.

(5) Fuel savings are estimated by taking maximum likely fuel savings listed herein (10%) over 124537-234914 km travelled per truck and average fuel mileage [Natural Resources Canada; *Fuel Efficiency Benchmarking in Canada’s Trucking Industry*, http://oee.nrcan.gc.ca/transportation/business/reports/884 (accessed Feb 9, 2010], and a current average Canadian fuel cost of $1.22 L-1 [http://www.gasbuddy.com (accessed Feb 9, 2012)].


