Metal Nanoparticles Immobilized on Basic Supports as Catalysts for Hydrogenation and Dehydrogenation Reactions of Relevance to Cleaner Fossil Fuels and Alternative Sources of Energy

Reena Rahi

Graduate Center, City University of New York
Metal Nanoparticles Immobilized on Basic Supports as Catalysts for Hydrogenation and Dehydrogenation Reactions of Relevance to Cleaner Fossil Fuels and Alternative Sources of Energy

by

REENA RAHI

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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

Dr. Roberto Sanchez-Delgado__________

Date  Chair of Examining Committee

Dr. Maria Tamargo__________

Date  Executive Officer

Dr. Maria Contel

Dr. Charles Drain

Dr. Lynn Francesconi

Dr. Andrei Jitianu

Supervisory Committee

THE CITY UNIVERSITY OF NEW YORK
Abstract

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Adviser: Roberto A. Sanchez-Delgado

We developed a series of catalysts, composed of metal nanoparticles immobilized on basic supports for the hydrogenation of heteroaromatics of relevance to cleaner fossil fuels and biodiesel, and for the dehydrogenation of heteroaromatics of relevance to hydrogen storage in organic liquids. Our catalyst design involves nanostructured catalysts composed of metal particles immobilized on basic supports capable of ionic mechanism that may avoid catalyst poisoning and enhance catalytic activity.

We prepared a new catalyst composed of Pd nanoparticles immobilized on MgO by NaBH₄ reduction of Na₂PdCl₄ in methanol in the presence of the support. TEM measurements revealed well-dispersed 1.7 nm Pd particles attached to MgO, also characterized by XPS, XRD and hydrogen pulse chemisorption measurements. The new catalyst is efficient for the hydrogenation of the heterocyclic ring of quinolines, as well as for the mild reduction of a variety of alkenes representative of fuel components, and the partial saturation of biodiesel.

In the second part, we switched our attention to ruthenium nanoparticles, with the aim of achieving higher activity and broader reactivity, supported on functionalized carbon nanotubes,
of higher surface area. Our second catalyst was prepared by first attaching pyridine groups to the surface of the nanotubes, and then depositing the metal particles by NaBH₄ reduction of RuCl₃·3H₂O. TEM, XRD and XPS analysis indicate the presence of 1.7 nm Ru(0) particles attached mainly to the surface of the nanotubes. The Ru/py-CNTs results in an unprecedentedly high activity for the selective hydrogenation of N-heteroaromatic compounds, with respect to other reported systems. The activity of this catalyst was extended also to plain aromatic compounds under mild conditions and to the challenging S-heteroaromatics under more forcing conditions.

Lastly, we evaluated the efficacy of the catalyst for the dehydrogenation of 1,2,3,4-tetrahydroquinoline, which was achieved with reasonable turnover frequencies under moderate conditions. The hydrogenation/dehydrogenation reactions thus establish a cyclic process of possible utility in hydrogen storage in organic liquids. We screened other substrate pairs that may be adequate for hydrogen storage, by computational study of the thermodynamics of dehydrogenation, which allowed us to identify other N-heterocycles that may prove useful in future studies.
Dedicated to my loving family
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# Table of Contents

Title Page ................................................................. i

Approval page ........................................................... iii

Abstract ........................................................................ iv

Dedication ..................................................................... vi

Acknowledgement ........................................................ vii

List of Symbols and Abbreviations ....................................... xiii

List of Figures .................................................................. xvi

List of Schemes .............................................................. xix

List of Tables ................................................................... xx

Chapter 1 Energy Outlook ...................................................... 1

1.1. Fossil Fuels ................................................................. 2

1.2. Biomass: an alternative to fossil fuels ................................. 4

1.3. H₂: a secondary source of energy .................................... 6

Chapter 2 General Introduction ............................................... 8

2.1. Hydrogenation as a means to cleaner fossil fuels ................. 8

2.2. Supported metal nanoparticles in hydrogenation catalysis ....... 9

2.3. Mechanisms of hydrogen activation by metals ................... 10

2.4. Organic liquids as a means to store hydrogen ................... 11

2.5. Mechanism of dehydrogenation of N-heteroaromatic compounds ... 12

2.6. Hypothesis and aims of this work .................................. 16

2.7. Our catalyst design ...................................................... 17
Chapter 3 Hydrogenation of quinolines, alkenes, and biodiesel by palladium nanoparticles immobilized on magnesium oxide .......................................................... 18

3.1. Introduction .............................................................................................................. 18

3.1.1. Fossil fuels upgrading ...................................................................................... 18

3.1.2. Catalytic hydrogenation in the production of clean fossil fuels ............ 19

3.1.3. Catalytic hydrogenation of alkenes and gasoline improvement ........... 21

3.1.4. Catalytic hydrogenation as a means to improve the oxidative stability of biodiesel ........................................................................................................ 22

3.2. Results and discussion ....................................................................................... 24

3.2.1. Catalyst preparation and characterization ......................................................... 24

3.2.1.1. Preparation ................................................................................................... 24

3.2.1.2. TEM measurements .................................................................................... 24

3.2.1.3. ICP-AES .................................................................................................... 26

3.2.1.4. BET surface area, H₂ pulse chemisorption and temperature programmed reduction (TPR) experiments ................................................. 27

3.2.1.5. XPS analysis ............................................................................................... 29

3.2.1.6. XRD results ................................................................................................. 32

3.2.2. Catalytic hydrogenation ..................................................................................... 33

3.2.2.1. Hydrogenation of quinolines ..................................................................... 33

3.2.2.2. Hydrogenation of alkenes ......................................................................... 37

3.2.2.3. Partial hydrogenation of biodiesel .............................................................. 39

3.2.3. Catalyst recyclability ......................................................................................... 40

3.3. Conclusion ............................................................................................................. 42
3.4. Experimental .................................................................................................................. 42
  3.4.1. Materials ................................................................................................................. 42
  3.4.2. Synthesis of Pd/MgO ............................................................................................. 43
  3.4.3. TEM studies ........................................................................................................... 44
  3.4.4. XRD measurements ............................................................................................... 44
  3.4.5. XPS measurements ............................................................................................... 44
  3.4.6. Hydrogen pulse chemisorption ............................................................................. 45
  3.4.7. H$_2$-TPR analysis ................................................................................................. 45
  3.4.8. Catalytic tests ........................................................................................................ 45
    3.4.8.1. Hydrogenation of quinolines ............................................................................ 45
    3.4.8.2. Hydrogenation of alkene ................................................................................ 46
    3.4.8.3. Partial hydrogenation of alkene ...................................................................... 46
    3.4.8.2. Recycling experiments .................................................................................... 47

Chapter 4 Hydrogenation of N- and S-heteroaromatic and aromatic compounds and
dehydrogenation of N-heterocycles by ruthenium nanoparticles immobilized
on pyridine-functionalized carbon nanotubes ................................................. 48

  4.1. Introduction ................................................................................................................ 48
    4.1.1. New catalytic system for hydrogenation of heteroaromatic and
           aromatic compounds .............................................................................................. 48
    4.1.2. Dehydrogenation of organic liquids for hydrogen storage
           applications ........................................................................................................... 49
  4.2. Results and discussion ............................................................................................... 50
    4.2.1. Catalyst preparation and characterization ......................................................... 50
4.2.1.1. Ruthenium nanoparticles on acid-oxidized carbon nanotubes (Ru/AO-CNTs) .................. 50
4.2.1.2. Synthesis and characterization of pyridine functionalized carbon nanotubes (py-CNTs) .... 51
4.2.1.3. Synthesis of 5 wt% Ru/py-CNTs ................. 55
4.2.1.4. TEM measurements of 5 wt% Ru/py-CNTs ...... 56
4.2.1.5. XPS analysis ........................................... 57
4.2.1.6. XRD results of 5 wt% Ru/py-CNTs ............. 60
4.2.2. Catalytic tests .............................................. 60
4.2.2.1. Hydrogenation of quinoline over Ru/AO-CNTs .. 60
4.2.2.2. Hydrogenation of quinoline over Ru/py-CNTs ... 61
4.2.2.3. Hydrogenation of other N-heteroaromatics ....... 64
4.2.2.3. Hydrogenation of other S-heteroaromatics ....... 66
4.2.2.5. Hydrogenation of arenes ............................ 67
4.2.2.1.6. Catalyst recyclability test of 5 wt% Ru/py-CNTs .................. 69
4.2.2.1.7. Possible hydrogenation mechanism ......................... 69
4.2.2.1.8. Dehydrogenation of 1,2,3,4-tetrahydroquinoline ............. 73
4.2.2.1.9. Computational studies on alternative hydrogenation/dehydrogenation substrate pairs .................... 76
4.3. Conclusions .................................................................................................................. 83

4.4. Experimental ............................................................................................................. 87

4.4.1. Materials .............................................................................................................. 87

4.4.2. Catalyst preparation and characterization ......................................................... 88

4.4.2.1. Synthesis of pyridine functionalized carbon nanotubes (py-CNTs) ............. 88

4.4.2.2. Synthesis of Ru/py-CNTs ................................................................. 88

4.4.2.3. TEM studies ............................................................................................... 89

4.4.2.4. XPS measurements .................................................................................... 89

4.4.2.5. XRD measurements .................................................................................... 90

4.4.3. Catalytic tests .................................................................................................... 90

4.4.3.1. Hydrogenation of N-heteroaromatics ................................................. 90

4.4.3.2. Recycling experiments of 5 wt% Ru/py-CNTs ... 90

4.4.3.3. Dehydrogenation of N-heteroaromatics ............................................ 91

4.4.4. Computational methods .................................................................................... 91

Bibliography .................................................................................................................... 93
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
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<tr>
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</tr>
</tbody>
</table>
List of Figures

Figure 1-1. Energy sources and their percent consumption in the U.S. .......................... 1
Figure 1-2. A schematic diagram of refinery processes. ................................. 2
Figure 1-3. Crude oil composition. ................................................................. 4
Figure 2-1. Mechanisms of H₂ activation. ...................................................... 10
Figure 2-2. Noyori’s catalysts (top), transition state in ionic hydrogenation of polar bonds does not require binding of the substrate to the metal prior to hydrogen transfer (bottom). ........ 11
Figure 2-3. Heterolytic splitting of hydrogen on Ru/PVPy. ............................. 12
Figure 2-4. Our catalyst design: the nanostructure composed of metal nanoparticles and basic sites for ionic hydrogenation mechanism. ............................... 17
Figure 3-1. Total energy consumption in the U.S. by source, 2012. ................... 18
Figure 3-2. HDN of quinoline involves hydrogenation prior to C-N bond scission. .......... 20
Figure 3-3. Main product of crude oil refining. ................................................ 21
Figure 3-4. Partial hydrogenation of methyl esters catalyzed by Rh/TPPTS complexes. .... 27
Figure 3-5. Transmission electron micrographs of a freshly prepared sample (top) and used sample (bottom) of 1 wt% Pd/MgO with corresponding particle size distribution histogram. ... 25
Figure 3-6. Transmission electron micrographs of a freshly prepared sample of 5 wt% (top) and 10 wt% (bottom) of Pd/MgO with corresponding particle size distribution histograms. ....... 26
Figure 3-7. H₂-TPR profile of the three Pd/MgO catalysts and MgO support. ............ 29
Figure 3-8. XPS survey scan of a fresh sample of 1 wt% Pd/MgO using Mg Kα excitation as X-ray source. ................................................................. 30
Figure 3-9. X-ray photoelectron microscopy of 10 wt% Pd/MgO. .......................... 31
Figure 3-10. Pd 3d XPS spectra of a fresh sample of 5 wt % Pd/MgO. ..................... 31
Figure 3-11. Powder x-ray diffraction pattern 1, 5 and 10 wt% Pd/MgO. .......................... 32
Figure 3-12. Hydrogenation of quinoline catalyzed by 1 wt% Pd/MgO (150 °C, 40 atm H₂; \( n_Q : n_{Pd} = 1000 \)). Left: reaction profile, in THF; \( \Delta \) : Quinoline; \( \blacktriangle \) : 1,2,3,4-tetrahydroquinoline); right: linear plot of H₂ uptake used to calculate TOF_{init} in hexane. ................................................................. 34
Figure 3-13. Hydrogenation of quinoline over 1 wt% Pd/MgO (\( n_{sub} : n_{Pd} = 1000 \) in THF). Left: Influence of pressure on hydrogenation rate, 150 °C; Right: Effect of temperature on hydrogenation rate at 40 atm. ................................................................. 35
Figure 3-14. Comparison of 1 wt% Pd/MgO with commercial catalysts for hydrogenation of quinoline to \(^1\)THQ at 150 °C and 40 atm H₂; \( n_{sub} : n_{Pd} = 1000 \) hexane. .................................................. 36
Figure 3-15. GC/MS analysis of the composition of crude biodiesel and hydrogenated biodiesel before (left) and after (right) hydrogenation over Pd/MgO at 100 °C and 1 atm H₂. ............ 40
Figure 3-16. Activities of the 1 wt% Pd/MgO catalyst (100 mg) in three consecutive runs of hydrogenation; Left: cyclohexene, r.t., 10 atm H₂; Right: quinoline, 150 °C, 40 atm H₂. ........ 41
Figure 4-1. TEM micrograph (left), and Ru 3p XPS spectra (right) of fresh 5 wt% Ru/AO-CNTs. .................................................................................................................. 51
Figure 4-2. Heterolytic splitting of H₂ and ionic hydrogen transfer to polar bonds, assisted by the basic sites of the support on Ru/PVPy catalyst. ................................................................. 52
Figure 4-3. XPS survey scans of CNTs (top), and narrow scan in the N 1s region of py-CNTs (bottom). .................................................................................................................. 54
Figure 4-4. Transmission electron micrographs and particle size distribution histogram of a fresh sample of 5 wt% Ru/py-CNTs. ................................................................. 57
Figure 4-5. XPS survey scan of a fresh sample of 5 wt% Ru/Py-CNTs. .............................. 58
Figure 4-6. C 1s and Ru 3d XPS spectra of a fresh sample of 5 wt% Ru/py-CNTs. .............. 59
Figure 4-7. Ru 3p\textsubscript{1/2} and Ru 3p\textsubscript{3/2} XPS spectra of a fresh sample of 5 wt% Ru/py-CNTs. ....... 59

Figure 4-8. X-ray diffraction pattern of (a) py-CNT, and (b) fresh 5 wt% Ru/Py-CNTs. ........... 60

Figure 4-9. Hydrogenation of quinoline catalyzed by 5 wt% Ru/Py-CNTs (150 °C, 40 atm H\textsubscript{2}; \(n_\text{Q} : n_\text{Ru} = 1000\)): reaction profile, P vs. t graph (left); slope obtained from the linear section of the plot of P vs. t (right). .......................................................... 61

Figure 4-10. Catalytic activity of 5 wt% Ru/py-CNTs during recycling experiments. ........... 69

Figure 4-11. Possible hydrogen activation mechanisms on 5 wt% Ru/py-CNTs. ................... 70

Figure 4-12. The dual-site substrate-dependent mechanism involving both heterolytic and homolytic pathways. ......................................................... 71

Figure 4-13. Possible dehydrogenation (green arrows) and hydrogenation (black arrows) mechanism of \textsuperscript{1}THQ and quinoline, respectively, over 5 wt% Ru/py-CNTs. ................. 76

Figure 4-14. List of [6,6] fused rings with the number of nitrogen atoms with one, and two nitrogen at atoms at ortho, meta and para positions. .................................................. 78

Figure 4-15. List of [6,6] fused rings with the number of nitrogen atoms at ortho, meta and para positions. ...................................................... 78

Figure 4-16. List of five membered rings with the number of nitrogen atoms ranging from 1–3. ........................................................................ 79

Figure 4-17. List of [6,5] fused rings with the number of nitrogen atoms ranging from 1–3. ... 79

Figure 4-18. TOF\textsubscript{init} for the hydrogenation of quinoline by 1 wt% Pd/MgO, 5 wt% Ru/AO-CNTs, and 5 wt% Ru/py-CNTs at 150° C and 40 atm H\textsubscript{2}. ........................................ 85

Figure 4-19. Hydrogenation-dehydrogenation of quinoline-1,2,3,4-tetrahydroquinoline, respectively, over 5 wt% Ru/py-CNTs for hydrogen storage applications. .......................... 86

Figure 4-20. Comparison of the highest normalized \(\Delta G_{150 \degree C}\) values for each ring system. ...... 87
List of Schemes

Scheme 2-1. Hydrodearomatization (HDA) process for aromatic hydrocarbons. ......................... 9

Scheme 2-2. An overall schematic of liquid storage material distribution and utilization for transportation applications (Figure from Crabtree, 2008). ......................................................... 15

Scheme 2-3. Net reaction scheme for dehydrogenation and hydrogenation of H₁₂-NEC and NEC, respectively. ................................................................. 16

Scheme 3-1. The synthesis of Pd/MgO. .................................................................................... 24

Scheme 4-1. Overall scheme of carbon nanotubes functionalization followed by metal deposition. .................................................................................. 53

Scheme 4-2. Functionalization of carbon nanotubes with pyridine groups using 4-aminopyridine and sodium nitrite in hydrochloric acid. ......................................................... 53

Scheme 4-3. Ruthenium metal deposition on pyridine functionalized carbon nanotubes using sodium borohydride. .................................................................................. 56

Scheme 4-4. Proposed mechanism for hydrogenation of quinoline by Pd/MgO, Ru/PVPy, and Ru/MgO catalysts for the coordination of quinoline to the catalyst exclusively through –N of the heterocycle......................................................... 62

Scheme 4-5. Hydrogenation of benzothiophene at 200 °C and 50 atm H₂ over 5-wt% Ru/py-CNTs.................................................................................................................. 66

Scheme 4-6. Hydrogenation-dehydrogenation of N-heteroaromatic compound by catalyst. ..... 73

Scheme 4-7. Dehydrogenation of 1,2,3,4-tetrahydroquinoline at 150 °C in the presence of 1-octadecene. ........................................................................................................... 74
List of Tables

Table 3-1. Physical and chemical adsorption measurements results. ...................................... 28
Table 3-2. Hydrogenation of quinolines over 1 wt% Pd/MgO\textsuperscript{a}. ........................................... 37
Table 3-3. Hydrogenation of selected alkenes over 1 wt% Pd/MgO\textsuperscript{a}. ............................... 38
Table 4-1. Hydrogenation of N-heteroaromatics over 5 wt% Ru/Py-CNTs\textsuperscript{a} after 2 h. ............. 63
Table 4-2. Comparison of catalytic activities of different catalysts for the hydrogenation of quinoline. ......................................................................................................................... 64
Table 4-3. Hydrogenation of arenes over 5 wt% Ru/py-CNTs\textsuperscript{a} after 2 h. ................................. 68
Table 4-4. Comparison of catalytic activities of other ruthenium catalysts prepared by our group for the hydrogenation of substituted arenes. ................................................................. 68
Table 4-5. Dehydrogenation of 1,2,3,4-tetrahydroquinoline at 150 °C after 4h. ......................... 74
Table 4-6. Thermodynamic data (\(\Delta G_{150{\text{C}}}\)) per \(H_2\) molecule released as obtained from B3LYP/cc-pVDZ calculations. ................................................................. 88
Chapter 1

Energy outlook

With the growing demand of energy in the United States and worldwide, there exists a need to improve and advance traditional (e.g. fossil fuels) and non-traditional (e.g. biodfuels, H₂) sources of energy. These sources are divided into two main categories: non-renewable and renewable (Figure 1-1). As the name suggests, non-renewable energy comes from sources that cannot be replenished and therefore, will eventually run out. Non-renewable energy includes fossil fuels and nuclear energy, and they currently meet > 90 % of our energy demands.

![Energy sources and their percent consumption in the U.S.](image)

Figure 1-1. Energy sources and their percent consumption in the U.S.

Renewable energy, on the other hand, can be replenished and therefore, is considered environment friendly and sustainable. It includes of biomass (wood and wood waste, municipal
solid waste, landfill gas and biogas, ethanol, and biodiesel), hydropower (water), geothermal, wind, and solar. In the U.S. only 9 % of our energy consumption is provided by renewable sources.

1.1. Fossil Fuels

Fossil fuels are retrieved from the ground in the forms of solid (coal), liquid (crude oil), and gas (natural gas and propane). Crude oil is the major source of electricity and transportation fuels in the U.S. After its retrieval from the ground, crude oil is processed in a refinery where it is separated by physical and chemical methods into major fractions, including gasoline, diesel, jet fuel, and other products. Oil refineries carry out three basic operations (Figure 1-2): 1) separation, 2) conversion, and 3) treatment.[1] During separation, fractions are distilled and isolated based on their molecular weights and boiling points, heavier fractions (gas oils) are collected at the bottom, whereas medium (kerosene, diesel oil, etc.) and lighter (gasoline vapors, and liquid petroleum gas) are recovered at the top of the refinery tower, respectively.

![Figure 1-2. A schematic diagram of refinery processes.](image-url)
Medium and heavy gas oil collected from the bottom of the distillation tower, then go through the conversion process. Through this high pressure and high temperature treatment, also known as cracking, heavy molecules are broken and rearranged to obtain lighter molecules that make up diesel. The gaseous, small molecule byproducts that result from cracking are then alkylated in the presence of a catalyst to produce higher quality gasoline. The lighter liquid fractions are kerosene (C6-C16) and naphtha (C5-C12), which are the bases for the manufacture of jet fuel and gasoline, respectively. Lastly, the end products are carefully combined during the treatment step in a variety of proportions to achieve blends with desired levels of octane rating, vapor pressure, etc.

Crude oil mostly consists of alkanes, alkenes, and aromatics plus small amounts of heteroaromatics and some other chemicals, as shown in Fig 1-3.\textsuperscript{[2]} The combustion products of these compounds, CO\textsubscript{2}, CO, NO\textsubscript{x}, and SO\textsubscript{2} are harmful to the environment and human health.\textsuperscript{[3]} In 1990, the Federal government mandated the Clean Air Act in cities with high levels of smog.\textsuperscript{[4]} It requires that gasoline must be blended to produce reformulated gasoline (RFG) that burns more cleanly and results in reduced toxic emissions. According to the Environmental Protection Agency (EPA), as a result of introducing RFG about 75 million people breathe cleaner air.\textsuperscript{[3]} Similarly, sulfur contents in fuels have also been regulated by both the U.S. and the EU governments, to maximum levels around 10–15 ppm S.\textsuperscript{[5]} In order to achieve such low levels of heteroatoms, refinery feedstocks must be subjected to hydrotreatment, a process that uses hydrogen under pressure and catalysts composed of sulfided Co/Mo or Ni/Mo supported on alumina, to break C-S bonds (hydrodesulfurization, HDS), and C-N bonds (hydrodenitrogenation, HDN) thereby producing cleaner hydrocarbons, and releasing H\textsubscript{2}S and NH\textsubscript{3} as byproducts. These will be discussed in more detail in the following chapters.
1.2. **Biomass: an alternative to fossil fuels**

Biomass, a renewable energy source comes from plants (e.g. wood, crops) and animals (e.g. manure, trash). Since its sources can be regrown, it is considered a better alternative to fossil fuels. Biomass can be burned to release energy (for example, wood), or converted to liquid fuels (biofuels), such as ethanol and biodiesel, or bio-oils further processed into hydrocarbon mixtures, to be used as transportation fuels. Since biofuels come from plants, they are considered to have a negative CO₂ impact; plants absorb the CO₂ released during ethanol and biodiesel combustion as they grow and produce these biofuels. Moreover, unlike fossil fuels, they are non-toxic and biodegradable.

Ethanol, which is produced from corn, sugar cane and algae, can be used pure, or in petroblends. A target set by the U.S. government requires 36 billion gallons of ethanol to be used by the year 2022. The use of ethanol as fuel is increasing and becoming more common in the U.S. since nearly all gasoline is blended with some quantity of ethanol to improve its quality.

Biodiesel, another form of liquid biofuel, is produced from vegetable oils, fats, and greases. Due to its environment-friendly nature, the U.S. government has provided substantial
subsidies to promote the use of biodiesel either as pure or in petrodiesel-blends. In 2012, 870 million gallons were consumed, an increase from 10 million gallons in 2001. In the U.S. most of the biodiesel produced comes from soybean oil, a product of animal feedstock, or from recycled grease, a byproduct of cooking oil used in restaurants.

In other parts of the world, however, large areas of natural vegetation and forests have been wiped clean to grow plants, such as soybeans, corn, and sugarcane to produce biodiesel and ethanol in place of food crops. This has had a direct impact on food costs. As a result, growing crops for biofuels has raised some controversy and ethical dilemma. To circumvent this issue, the U.S. government has invested in discovering alternative ways of producing biodiesel and ethanol. For example, in addition to using grease, algae can be employed to yield biodiesel, whereas, waste paper can be used to make ethanol.

Another example of renewable energy is biomass waste, such as lignocellulose biomass which comes from wood, agricultural waste, or grass. It is inexpensive and abundant, and since it does not compete with food crops for land and water resources, it is a better alternative to biodiesel. Lignocellulose biomass can be converted to an energy source through pyrolysis (thermal decomposition), during which the biomass is heated rapidly to high temperatures (500 °C) in the absence of oxygen, followed by quick cooling of the vapors to achieve fluid liquids (bio-oils). Compared to fossil fuels, bio-oils, however contain high levels of oxygen (up to 50%), since they are complex mixtures of carboxylic acids and esters, ethers, alcohol and polyols, aldehydes, and ketones, and therefore, have a lower heat value than fossil fuels. To remove oxygen and yield liquid hydrocarbons and water, hydrodeoxygenation (HDO) is generally applied as a part of hydrotreatment subsequent to pyrolysis. Common catalysts for hydrotreatment of fossil fuels, e.g. H2S stabilized Co/Mo or Ni/Mo on alumina, may also be
employed for HDO of bio-oils, but are undesirable due to the presence of sulfur that may end up in bio-oils as a contaminant. Supported noble metals (Ru, Rh, Pd, and Pt) and other late transition metals (Ni and Cu) are a promising alternative and have shown to promote HDO of bio-oils.[8] However, further research is needed to achieve lower oxygen contents in bio-oils to fully harness their potential in heating and transportation fuel applications.

1.3. \textit{H}_2: a secondary source of energy

In addition to renewable and non-renewable energy, there is another type of energy source: hydrogen (H\textsubscript{2}). Unlike renewable (\textit{e.g.} biofuels) and non-renewable (\textit{e.g.} fossil fuels) sources of energy, hydrogen is a secondary energy source. It stores and carries the energy produced by the primary sources of energy, such as fossil fuels and biomass.[9]

With the environmental issues related to fossil fuels, and ethical dilemmas associated with the production of biodiesel from food sources, the need for alternative sources of energy is critical. Hydrogen is a particularly promising proxy as an energy carrier due to its high abundance in the universe (H\textsubscript{2}O, hydrocarbons such as fossil fuels and biomass, \textit{etc.}), and its ability to burn without forming any noxious gases, making it a ‘green’ fuel.[10] In addition, H\textsubscript{2} has the largest energy content per kilogram compared to all other fuels and can be used with the current energy infrastructure, making it economically desirable.[11]

To obtain hydrogen from hydrocarbons, such as methane (CH\textsubscript{4}), steam-reforming is employed. In this process, methane gas is reacted with water at high temperatures and pressures in the presence of a metal catalyst, to produce hydrogen gas, and carbon monoxide or carbon dioxide.[12] However, due to the formation of greenhouse gases, this method is considered harmful to the environment. Electrolysis of water, on the other hand, is considered a ‘cleaner’ procedure since it does not result in the emission of greenhouse gases. In this process, water is
split into H$_2$ and O$_2$ gases. Though water-splitting processes are expensive at present, extensive research is being done to develop economical technologies.$^{[9]}$

As an energy carrier, hydrogen can either be used: 1) in fuel cells to produce electricity to power electric cars and homes, or 2) to fuel conventional automobiles using internal combustion engines (ICE). Fuel cells produce electricity from chemical energy by reacting H$_2$, and O$_2$ from air.$^{[13]}$ Hydrogen used in fuel cells can either be pure hydrogen gas or can be obtained from hydrocarbons (e.g. methane or gasoline) through a fuel reformer. With water as the only byproduct, the use of fuel cells to generate energy from hydrogen produces no toxic gas emissions and therefore, is extremely environment friendly. Similarly, when hydrogen (liquefied) is burned in air in an internal combustion engine, it produces water as the only product, making hydrogen the cleanest, safest energy carrier.
Chapter 2

General Introduction

2.1. Hydrogenation as a means to cleaner fossil fuels

To reduce the contents of alkenes, aromatics, and small amounts of heteroaromatics present in crude oil, catalytic hydrogenation can be utilized. In industrial settings, heterogeneous catalysts are employed primarily, due to their ability to withstand harsh reaction conditions, as well as the ease of recovery associated with solid catalysts for recycling purposes. Hydrotreating is one of the most important processes in oil refining; crude oil is reacted with hydrogen over appropriate catalysts in order to remove undesirable heteroatoms, mainly N, S, and O, through hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodeoxygenation (HDO) reactions, respectively. The most common catalysts used in petroleum refining include sulfided catalysts, such as NiMo, NiW, and CoMo supported on alumina.\(^{[14]}\) These catalysts, however, require high temperatures (300-400 °C) and pressures (50-100 atm) to achieve HDN and HDS. Although the detailed mechanisms of HDN and HDS continue to be debated, there is a general agreement that hydrogenation of heterocycles and/or carbocycles are key steps preceding, and possibly limiting, the extrusion of the heteroatoms. Therefore, the discovery of new and improved hydrogenation catalysts for aromatic and heteroaromatic substrates is of much importance. Under hydrotreating conditions with conventional metal sulfide catalysts hydrogenation of aromatic compounds is exothermic and reversible (Scheme 2-1), and therefore, thermodynamically unfavorable under the required reaction conditions. As a result of the equilibria involved, these catalysts cannot achieve complete conversion to saturated species.
Scheme 2-1. Hydrodearomatization (HDA) process for aromatic hydrocarbons.

Supported noble metal catalysts (e.g. Pt, Pd) on the other hand, can function at mild reaction conditions. However, they easily get poisoned by small amounts of nitrogen and sulfur containing compounds present in the feedstock.\cite{14-15} Poisoning occurs when the heteroatom (in the substrate or the product) forms a strong bond to the active site on the catalyst and does not dissociate at the end of the reaction and as a result, the catalyst becomes inactive. Therefore, the use of supported noble metal catalysts in hydrotreatment is limited.

2.2. **Supported metal nanoparticles in hydrogenation catalysis**

A particularly promising class of hydrogenation catalysts includes supported metal nanoparticles. In recent times metal nanoparticles (NPs) have been studied extensively. They exhibit much higher catalytic activity than their bulk counterparts under mild reaction conditions due to their large surface area; they are also attractive in Green chemistry for their recyclability.\cite{16} However, in the absence of a support, nanoparticles are prone to aggregation. In order to utilize the unique size-related features of nanoparticles and prevent aggregation, stabilization is required. Nanoparticles are generally stabilized by ligands, surfactants or ionic liquids (ILs) or immobilized on solid supports.\cite{16a} For catalytic purposes, solid supported metal nanoparticles are more advantageous due to their stability under strong reaction conditions, as well as the ease of recovery of solid catalysts for recycling purposes.

Of particular relevance to our work, the use of palladium nanoparticles immobilized on different supports (hydroxyapatite,\cite{17} tannins,\cite{18} hyperbranched aramids\cite{19}) has been reported
for the hydrogenation of N-heteroaromatics, such as quinoline, at various reaction conditions with a wide range of activities. Ruthenium nanoparticles supported on various supports (e.g. hydroxyapatite,[20] silica,[21] and polymer[22]) have also shown to hydrogenate N-heteroaromatics with different levels of activity. In these studies, the only role of support is generally to prevent aggregation and make the catalyst recovery easy for recycling. No examples of catalytic materials where the support takes active part in hydrogenation catalysis were found.

2.3. Mechanisms of hydrogen activation by metals:

Hydrogen activation by metals occurs through three general pathways (Figure 2-1).[23] (i) homolytic splitting of H₂ into two H atoms (Eq. 1); (ii) oxidative addition of H₂ to form a metal dihydride (Eq. 2); and (iii) base-assisted heterolytic cleavage of H₂ into H⁺ and H⁻ (Eq. 3). In heterolytic cleavage, the base E acting as a proton trap may be an external reactant, or a ligand, or a site in the support.

\[ M-M + H_2 \rightarrow M-H \]  
\[ M - H + H \rightarrow M-M \]  

\[ M - E + H_2 \rightarrow M-E \]  

**Figure 2-1.** Mechanisms of H₂ activation.

An example, where ionic H₂ activation is the key step, is the homogeneous asymmetric hydrogenation of polar bonds by Noyori’s catalysts (Figure 2-2, top).[24] Noyori’s catalysts, however, only work for certain substrates, not including aromatics. In ionic hydrogenation
mechanisms in solution, the substrate does not directly bind to the metal. Instead, the hydrogen transfer occurs through outer sphere coordination to the protonated base and the hydride on the metal center (Figure 2-2, bottom left). The amine (–NH₂) in the ligand plays an important role in the reaction. Its presence increases the reactivity of the catalyst by promoting the heterolytic splitting and capturing the resulting proton. As shown in Figure 2-2 (bottom right), a pericyclic 6-membered ring is formed, followed by the Ru metal donating a hydride, and the NH₂ ligand supplying the proton to the substrate, simultaneously.

Figure 2-2. Noyori’s catalysts (top), transition state in ionic hydrogenation of polar bonds does not require binding of the substrate to the metal prior to hydrogen transfer (bottom).

This mechanism of H₂ activation and transfer is now very common in solution, but it is extremely rare on metallic surfaces. Unsupported RuS₂, to the best of our knowledge, is the only example for which there is direct experimental evidence (solid-state ¹H NMR at 100 °C) for the
formation of hydride species and –SH groups. This type of mechanism on a solid surface can be of great use in HDN and HDS reactions to avoid poisoning caused by the N– and S–species, since there is no direct binding between the active metal site and the substrate.

Recently, Fang et al. in our laboratory have demonstrated an unprecedented dual-site substrate-dependent mechanism using ruthenium nanoparticles supported on poly(4-vinylpyridine) Ru/PVPy. Metal nanoparticles with adjacent basic sites (Ru/PVPy) promote heterolytic splitting of hydrogen (Figure 2-3), and not only improve the catalytic activity but also avoid poisoning, since the substrate does not bind directly to the active metal site, rather undergoes an outer sphere coordination mechanism.

**Figure 2-3.** Heterolytic splitting of hydrogen on Ru/PVPy.

Building a nanostructure that by incorporating small metallic centers surrounded by strongly basic units of the support can thus be envisaged as a new way of avoiding poisoning of solid catalysts by substrates or products.
2.4. Organic liquids as a means to store hydrogen

With limited sources of fossil fuels that are bound to eventually run out, and the harmful effects of fossil fuel byproducts, alternative sources of energy are being explored extensively. Amongst these, hydrogen is a promising proxy as an energy carrier, as was mentioned in the previous chapter, due to its high abundance in the universe, its ability to burn without forming any noxious gases, making it a ‘green’ fuel,[27] and the fact that H\textsubscript{2} has the largest energy content per kilogram compared to all other fuels.[28]

For transportation (automobile) purposes, H\textsubscript{2} can be used as an energy carrier in either an internal combustion engine (ICE) or in fuel cells.[29] Among the many challenges related to optimizing H\textsubscript{2} as an energy supplier, storage is most crucial. The Department of Energy (DOE) requirements dictate that the hydrogen storage carrier must have storage capacity of $\geq$ 5.5 wt\% H\textsubscript{2}, calculated by the mass of H\textsubscript{2} liberated over the mass of hydrogenated material.[30] For transportation purposes, H\textsubscript{2} can be stored on the vehicles, generally, by five different methods: 1) high pressure tanks, 2) cryogenic methods, 3) complex hydrides, 4) solid materials with H\textsubscript{2} adsorbed, and 5) hydrogen storage in liquid organics.[28\textsubscript{a}, 29]

The use of high pressure tanks and cryogenic methods is unsuitable for commercial applications, due to the limits set by DOE (6.5 wt \% and 62 kg H\textsubscript{2} m\textsuperscript{–3} system capacity at room temperatures and 100 atm) for on-board storage systems. These methods of storage can be extremely dangerous, especially in the cases of motor collisions, and can lead to high costs in the forms of human life and infrastructure damages. Complex hydrides on the other hand, do not require high pressures and temperature to store and release H\textsubscript{2}, examples of which include light metal complex hydrides (e.g. MgH\textsubscript{2}, NaAlH\textsubscript{4}, and Mg(BH\textsubscript{4})\textsubscript{2}) and chemical hydrides (e.g. NaBH\textsubscript{4}, C\textsubscript{10}H\textsubscript{18}, and NH\textsubscript{3}BH\textsubscript{3}). These hydrides have a high density of hydrogen; however, they
generate hydrogen through chemical reaction and therefore, may not be ideal in transportation vehicles due to the lack of reversibility.\[27] The fourth method of storing hydrogen on solid materials has been researched extensively but still need further improvements in hydrogen desorption capabilities. Few examples of these include carbon materials, metal organic frameworks (MOFs), and porous materials.\[31]

The fifth type of hydrogen storage method includes organic liquids. They are much more attractive for hydrogen storage for transportation fuel purposes, and are more advantageous over solid storage materials. Liquid fuels can be delivered to and stored at a fuel station, and pumped into motor vehicles similar to gasoline, and therefore, no significant changes to the infrastructure (i.e. gas stations, vehicles) are required, as shown in Scheme 2-2.\[29] Small aliquots from the stored liquids can then be pumped into the catalytic dehydrogenation chamber for heating to the desired temperatures at any given time, in order to liberate the desired amount of hydrogen to power the engine. This eliminates the dangers associated with having large quantities of hot, reactive organic liquids on-board during collisions. After dehydrogenation, spent storage material would move back into the fuel tank (separated from the fresh materials to avoid mixing), while fresh material pumps into the catalytic chamber to be used. The used-material would then be brought back to the fuel station to be replaced by fresh storage materials. The hydrogenation of liquid materials would take place at an industrial facility. Trucks used for delivering fresh storage materials to fuel stations, would also pick up the spent materials and bring it back to the industrial facility to be hydrogenated. The ease of handling and delivery makes liquid storage materials a safer choice.

Moreover, unlike solid materials, liquid storage materials provide complete reversibility and recyclability. Studies suggest that N-heteroaromatic compounds are most promising as liquid
organic hydrogen carriers.\textsuperscript{[29, 32]} Amongst these \textit{N}-ethylcarbazole (NEC)/dodecahydro-\textit{N}-ethylcarbazole (H\textsubscript{12}-NEC) have shown the most potential as hydrogen carrier due to their hydrogenation/dehydrogenation capabilities at mild conditions (150–200 °C), and storing capacity of 5.8 wt\% H\textsubscript{2}.\textsuperscript{[33]} However, NEC is a solid below 68 °C, and therefore, its transportation is a challenge. Therefore, there exists a need to discover other organic compounds that may be used to store and release hydrogen at mild conditions.

\textbf{Scheme 2-2}. An overall schematic of liquid storage material distribution and utilization for transportation applications.

2.5. \textit{Mechanism of dehydrogenation of N-heteroaromatic compounds}

Dehydrogenation over transition metal catalyst can be used to release H\textsubscript{2} from N-heteroaromatic compounds, some examples of which include: Pd/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{[34]} and Pd/SiO\textsubscript{2}\textsuperscript{[30]}. Dehydrogenation of dodecahydro-\textit{N}-ethylcarbazole (H\textsubscript{12}-NEC) to \textit{N}-ethylcarbazole (NEC) yields 6 moles of H\textsubscript{2}, as shown in Scheme 2-3. Both, experimental and theoretical studies confirm that the activation of
H$_{12}$-NEC proceeds through initial interaction of the hydrogen atoms at the $\alpha$-carbon of the five
membered ring.$^{[33, 35]}$

![Scheme 2-3](image)

**Scheme 2-3.** Net reaction scheme for dehydrogenation and hydrogenation of H$_{12}$-NEC and NEC,
respectively.

Based on the principle of microscopic reversibility, we hypothesize that a catalyst that is
able to hydrogenate N-heteroaromatics must also be capable of dehydrogenating the
Corresponding saturated compounds.

**2.6. Hypothesis and aims of this work**

*Our hypothesis is that a well-defined nanostructure consisting of metallic
particles with adjacent basic surface sites will promote high catalytic activity in
the hydrogenation of heteroaromatic substrates, most likely via heterolytic H$_2$
splitting and thereby prevent catalyst poisoning.*

The specific aims of this work are:

1) To synthesize and characterize nanostructured catalysts composed of metal particles (Pd and
Ru) immobilized on different supports with basic functionalities (magnesium oxide, pyridine
functionalized carbon nanotubes, and graphene oxide)
2) To study the catalytic properties of these materials in:

- Hydrogenation of heteroaromatics, aromatics and olefins
- Hydrogenation of polyunsaturated methyl esters to their monounsaturated counterparts
- Dehydrogenation of organic compounds

### 2.7. Our catalyst design

Our general design of nanostructured catalysts contain small metallic nanoparticles (specifically palladium and ruthenium) immobilized on different supports with basic functionalities. The metal nanoparticles and basic functional groups on the support are expected to work in synergy to activate hydrogen through heterolytic mechanisms. Such splitting of the $\text{H}_2$ molecule into $\text{H}^+$ and $\text{H}^-$ ions will enhance the efficacy of the catalyst by avoiding the possibility of poisoning, since the hydrogen transfer will occur through outer sphere ionic pathways and the substrate or product will not form a direct bond with the active metal sites. An illustration of our catalyst design is depicted in Figure 2-4, showing nanostructured metal particles immobilized on a support with basic functionalities.

![Illustration of catalyst design](figure)

**Figure 2-4.** Our catalyst design: the nanostructure composed of metal nanoparticles and basic sites for ionic hydrogenation mechanism.
Chapter 3

Hydrogenation of quinolines, alkenes, and biodiesel by palladium nanoparticles immobilized on magnesium oxide*

3.1. Introduction

3.1.1. Fossil Fuel upgrading

According to the U.S. Department of Energy, fossil fuels (petroleum, natural gas, and coal) are the major sources of energy (83%) used in the country and will continue to be so at least in the next several decades, despite the extensive development and deployment of new renewable and nuclear technologies (Figure 3-1).[36]


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**Figure 3-1** Total energy consumption in the U. S. by source, 2012.
However, there are two major issues with fossil fuel consumption: 1) the high demand for energy sources will result in an eventual exhaustion the natural reserves, and 2) fossil fuels are harmful to the environment, among several reasons, because of the high levels of air polluting nitrogen and sulfur containing compounds. Upon combustion, nitrogen and sulfur oxides are released into the atmosphere and eventually cause acid rain; removal of nitrogen and sulfur compounds from fuels is therefore crucial.\[37\]

Current laws impose severe limits on the levels of nitrogen and sulfur containing aromatics in fuels, which are unattainable with current refining technologies. The amounts of N-heteroaromatic and S-heteroaromatic compounds contents in fossil fuels are routinely reduced through hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) processes, both of which involve prehydrogenation of aromatic rings. These reactions are commonly achieved by use of sulfided CoMo, NiMo, and NiW catalysts,\[14\] which generally require high pressures and temperatures (50-100 atm, 300-400 °C); the thermodynamics do not favor hydrogenation under the reaction conditions, and as a result the conversion is limited. Supported noble metal catalysts, on the other hand, can function under milder conditions, but they are limited in their use due to their high susceptibility to poisoning by small amounts of N- or S-containing compounds present in refinery feeds,\[14-15\] which form very strong bond to the catalyst and do not dissociate at the end of the reaction.

3.1.2. Catalytic hydrogenation in the production of clean fossil fuels

Although many details of the complex reaction schemes involved in HDN remain controversial, there is agreement in that hydrogenation of both carbocyclic and heterocyclic rings are key steps that take place prior to C–N bond scission and nitrogen removal. For instance, Figure 3-2 shows a typical HDN mechanism for quinoline, a representative compound present in significant
concentrations in the middle oil distillates.\textsuperscript{[38]} Saturation of the heterocyclic ring is thought to be a prerequisite for heteroatom extrusion, and hydrogenation of the carbocyclic ring also takes place over conventional catalysts, leading to a mixture of denitrogenated products with various degrees of unsaturation, \textit{e.g.} \textit{n}-propylbenzene, \textit{n}-propylecyclohexene, and \textit{n}-propylcyclohexane. Besides its relevance in clean fuel manufacture, catalytic hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline (\textit{1THQ}) is of great interest also in the synthesis of pharmaceutical intermediates and in the production of agrochemicals and dyes.\textsuperscript{[17-18]}

\textbf{Figure 3-2.} HDN of quinoline involves hydrogenation prior to C-N bond scission.

Hydrogenation of quinoline can be carried out in homogenous liquid phase using coordination or organometallic precious-metal complexes (Rh, Os, and Ru), but the practical utility of such systems for large-scale applications is limited due to the difficulty in recovering the expensive metal catalyst from the solution. Some heterogeneous catalysts (like sulfided NiMo, NiW, and CoMo) can be used, but these catalysts require harsh conditions, and display low catalytic activity and/or poor selectivity. Therefore, there exists a need for highly efficient catalysts that
can hydrogenate N-heteroaromatics under mild conditions without being easily poisoned by the substrates or the products. In this Chapter we describe the synthesis and characterization of a new nanostructured Pd/MgO catalyst and its application to the hydrogenation of quinoline and related compounds.

3.1.3. Catalytic hydrogenation of alkenes and gasoline improvement

Gasoline, a product of the manufacture of the middle distillate of petroleum (naphtha) and a major product of crude oil refining, is the primary transportation fuel in the U.S. (Figure 3-3) With billions of gallons of consumption each year in the U.S. alone, there is a high demand for ways of purifying gasoline and achieving higher improved combustion properties.

![Figure 3-3. Main product of crude oil refining](image)

The octane number is a measure of the combustion performance of a fuel; the higher the octane rating, the better the fuel’s ability to withstand compression and therefore, the higher the performance. Gasoline is typically composed of C5-C8 hydrocarbons including about 30% of aromatics, 34% of alkanes, and 35% alkenes; the proportion of aromatics needs to be reduced for
environmental reasons and the alkene content must be lowered in order to avoid polymerization and wax formation during combustion. Catalytic hydrogenation is an efficient way to lower the aromatic and alkene contents in the fuels. However, oversaturation of these molecules also results in lower octane ratings; it is therefore essential that not all of the aromatics and olefins get hydrogenated; reformulated gasoline, for instance, must contain about 15% of alkenes. Moreover, the type of alkene present in reformulated gasoline is also important. Generally, the octane ratings increase with the decreasing size of the carbon chain length, and with an increase in the branching of carbon chains.[41] Therefore, the hydrogenation of olefins present in gasoline requires high selectivity towards unbranched, longer chain alkenes. In this chapter, we also describe a study of the catalytic hydrogenation of a set of olefins representative of components of gasoline using our Pd/MgO catalyst.

3.1.4. Catalytic hydrogenation as a means to improve the oxidative stability of biodiesel

In addition to cleaner fossil fuels, we are also interested in other sources of energy that may one day replace fossil fuels. Biodiesel, an interesting alternative to petroleum-based fuels, is generally produced by transesterification of vegetable oils catalyzed by strong base or acid, to produce mixtures of fatty acid methyl esters (FAMEs).[42] Biodiesel displays similar combustion properties, viscosity, and cetane number (a measure of combustion performance for petrodiesel and biodiesel, similar to the octane number for gasoline). However, unlike fossil fuels, biodiesel is renewable, non-toxic, sulfur free, and is considered to have a negative CO₂ balance, making it cleaner and safer for the environment. In addition, it can either be used as a single fuel or in petrodiesel blends as a transportation fuel in a standard combustion engine.

One of the challenges with current biodiesel production, however, is long-term storage. Biodiesel is made of mixtures of polyunsaturated FAMEs, and is highly prone to oxidative
processes during storage, as well as higher NO\textsubscript{x} production when blended with petro-diesel.\textsuperscript{[43]} Saturation of most but not all C=C bonds through partial hydrogenation in either the precursor oils or in the biodiesel has been proposed to improve the oxidative stability and decrease the NO\textsubscript{x} emissions.\textsuperscript{[44]} For example, Rh/TPPTS complexes [TPPTS = P(C\textsubscript{6}H\textsubscript{4}-m-SO\textsubscript{3}Na\textsubscript{3})] have been shown to partially hydrogenate biodiesel in a two-phase liquid system to achieve better storage stability. However, liquid phase catalysts are generally unsuitable for large-scale applications for which solid catalysts are much more desirable, since they allow easy separation and recovery while displaying high activity and selectivity for the partial hydrogenation of methyl esters.

Several catalytic systems have been reported for the hydrogenation of vegetable oils or biodiesel; for instance, metallic Ni suspended in oil can be used at 170-180 °C under atmospheric pressure;\textsuperscript{[45]} silica-supported Cu is active and selective at 180 °C and 20 atm H\textsubscript{2};\textsuperscript{[46]} Liquid biphasic systems based on rhodium with sulfonated triphenylphosphine ligands operate at 50-100 °C and 10 atm H\textsubscript{2};\textsuperscript{[47]} Palladium supported on alumina was employed as a catalyst in the partial hydrogenation of sunflower oil at 40 °C and 10 atm H\textsubscript{2}, as a pretreatment for biodiesel synthesis;\textsuperscript{[48]} other metal oxide supports, including MgO provided lower activities and/or selectivities. Recently, the partial hydrogenation of biodiesel catalyzed by Pd NPs dispersed in ionic liquids\textsuperscript{[49]} or Pd NPs supported on Al\textsubscript{2}O\textsubscript{3} in the presence of ionic liquids\textsuperscript{[50]} has been reported; these systems are efficient at room temperature but require high H\textsubscript{2} pressures (75 atm). In the last part of this Chapter we demonstrate the potential of our Pd/MgO catalyst for the partial hydrogenation of biodiesel under extremely mild conditions.
3.2. Results and discussion

3.2.1. Catalyst preparation and characterization

3.2.1.1. Preparation

The catalyst used in this study, composed of palladium nanoparticles supported on magnesium oxide (1 wt% Pd/MgO), was prepared by the room temperature reduction of Na₂PdCl₄ with excess NaBH₄ in methanol at room temperature in the presence of suspended MgO, which had been previously calcined at 500 °C in the air for 2 h, as shown in Scheme 3-1.

\[
\text{Na}_2\text{PdCl}_4 + \text{NaBH}_4 \xrightarrow{\text{MeOH, r.t.}, 500 \text{ºC}} \text{Pd(0)/MgO} + \text{NaCl} + \text{B}_2\text{H}_6
\]

Scheme 3-1. The synthesis of Pd/MgO.

As the reaction proceeded, the dark reddish brown solution became colorless and the initially white suspended solid changed to gray; after appropriate work up, the catalyst was stored under inert atmosphere. For comparison and characterization purposes, analogous materials containing ca. 5 wt% and 10 wt% Pd/MgO were prepared by using the same procedure described above, except for the amount of Na₂PdCl₄ employed. This method is reliable, technically simple using common commercially available materials, and highly reproducible.

3.2.1.2. TEM measurements

TEM analysis of the freshly prepared 1 wt% Pd/MgO solid (Figure 3-5, top) revealed the presence of highly dispersed Pd particles with a narrow size distribution on the surface of the support, with an average diameter of 1.7 ± 0.6 nm, calculated by measuring 350 particles chosen at random from several images. We also analyzed a sample of a catalyst after it had been used in
a quinoline hydrogenation run (Figure 3-5, bottom) at 150 °C and 40 atm H₂. The TEM micrograph of the used sample shows that the average Pd particle diameter remains essentially unchanged (1.6 ± 0.6 nm), although the particle size distribution is somewhat broader. These results indicate that the catalyst does not undergo sintering or other aggregation processes to an important extent under the harshest conditions employed for hydrogenation reactions.

![TEM micrograph](image)

**Figure 3-5.** Transmission electron micrographs of a freshly prepared sample (top) and used sample (bottom) of 1 wt% Pd/MgO with corresponding particle size distribution histogram.

Moreover, TEM analysis of analogous fresh 5 wt% and 10 wt% Pd/MgO (Figure 3-6, top and bottom, respectively), prepared by using the same procedure, except for the amount of metal salt,
revealed particle size distributions very similar to that of the 1 wt% material, with average diameters of 1.5 ± 0.5 nm and 1.8 ± 0.6 nm, respectively. This suggests that regardless of the amount of palladium present, our synthetic method is effective in producing uniform and well-dispersed particles.

**Figure 3-6** Transmission electron micrographs of a freshly prepared sample of 5 wt% (top) and 10 wt% (bottom) of Pd/MgO with corresponding particle size distribution histograms.

### 3.2.1.3. ICP-AES

To verify the Pd metal loading in all three catalysts, inductively coupled plasma atomic emission
spectroscopy (ICP-AES) was employed. Based on the analysis the exact composition of the three catalysts are 0.9 wt%, 4.4 wt% and 9.7 wt% Pd, respectively. For convenience, hereafter we use the nominal 1 wt%, 5 wt%, and 10 wt% Pd/MgO notation to represent the different solids; nevertheless, the actual metal loadings from the ICP-AES analyses were used to calculate the turnover frequency (TOF) values in the catalytic experiments described below.

3.2.1.4. BET surface area, $H_2$ pulse chemisorption and temperature programmed reduction (TPR) experiments

To gain further insight into the physical properties of the solids, the Brunaur-Emmett-Teller BET surface area was determined before and after the metal loading (see Table 3-1). The MgO support (after calcination at 500 °C for 2h) has a moderate specific surface area of 88 m$^2$/g, which is essentially retained (91 m$^2$/g) after deposition of 1 wt% Pd NPs onto the surface.

Pulse hydrogen chemisorption measurements revealed that 1 wt% Pd/MgO has 4.7 ± 0.4 % Pd metal dispersion. This indicates that only a small fraction of the Pd particles are located on the surface to produce sites capable of interacting with hydrogen, while most of the palladium incorporated in the solid probably gets adsorbed into pores and becomes inaccessible for catalysis. The metal dispersion values obtained from $H_2$ chemisorption experiments were subsequently used to calculate catalytic activities. Similar measurements were performed on commercial 5% Pd/SiO$_2$ and 5% Pd/Al$_2$O$_3$ catalysts, which were used for catalytic activity comparison, showing higher metal dispersion values of 11 ± 2% and 18 ± 2%, respectively.
Table 3-1. Physical and chemical adsorption measurements results.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m²/g)ᵃ</th>
<th>Metal dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>88</td>
<td>--</td>
</tr>
<tr>
<td>1% Pd/MgO</td>
<td>91</td>
<td>4.7 ± 0.4%</td>
</tr>
<tr>
<td>5% Pd/SiO₂</td>
<td>--</td>
<td>11 ± 2%</td>
</tr>
<tr>
<td>5% Pd/Al₂O₃</td>
<td>--</td>
<td>18 ± 2%</td>
</tr>
</tbody>
</table>

ᵃ Single-point measurement

To gather further information concerning the reducibility of the chemical species present on the surface of the Pd/MgO materials, H₂-TPR (temperature programmed desorption) experiments were carried out for 1wt%, 5 wt% and 10 wt% Pd/MgO, as well as for the MgO support itself. The TPR profiles for these four samples (Figure 3-7) showed no positive peaks indicative of hydrogen consumption, while the negative peaks observed around 360 K correspond to desorption from surface metallic Pd of the H₂ adsorbed at r.t. at the beginning of the analysis. The relative intensities of these peaks correlate with the amount of surface Pd in each sample, with the 10 wt% catalyst having the largest H₂ desorption peak. These TPR profiles demonstrate that no significant reduction processes take place within the temperature range 400–700 K and confirm that the Pd in our catalysts is exclusively or predominantly metallic (zerovalent), with no significant amounts of PdO being detected by any of the three methods employed. This is in contrast to what was observed for a similar Pd/MgO material prepared by impregnation, which showed a positive TPR peak at about 450 K ascribed to the presence of PdO.[51] The TPR data for our three Pd/MgO samples are consistent with the XRD and XPS results presented above, and confirm that the Pd in our catalysts is exclusively or predominantly
metallic (zerovalent), with no significant amounts of PdO being detected by any of the three methods employed.

![H2-TPR profile of the three Pd/MgO catalysts and MgO support](image)

**Figure 3-7.** H$_2$-TPR profile of the three Pd/MgO catalysts and MgO support

### 3.2.1.5. XPS analysis

The survey XPS scan of the 1 wt% Pd/MgO catalyst is shown in Figure 3-8. No peaks are observed around 200 eV (Cl 2$p$), indicating that the catalyst surface is free of Cl contamination from the preparation process, as opposed to what was observed for a similar Pd/MgO catalyst prepared by the impregnation method.[$^{51}$] The narrow scan in the Pd 3$d$ region displayed extremely weak signals because of the very low metal dispersion, as determined by H$_2$ pulse chemisorption, not allowing a reliable direct characterization by this method. Most of the metal particles must be located in pores where they are not detectable by XPS. Moreover, the 3$p$ region is highly interfered by large O peaks, making the deconvolution inapplicable.
However, satisfactory XPS data were obtained in the 3d region for the two analogous solids containing 10 wt% Pd/MgO (Figure 3-9) and 5 wt% Pd/MgO (Figure 3-10), which also display a higher proportion of metal particles on the surface, as shown by the hydrogen chemisorption measurements described above. The presence of metallic palladium on these surfaces is clearly indicated by the signals at 335.2 and 339.3 eV, which correspond to Pd(0) 3d5/2 and Pd(0) 3d3/2, respectively;[51] no evidence for any other Pd species was observed in the spectra of the two materials analyzed. With all preparation parameters being identical except for the amount of Pd precursor, it is reasonable to conclude that the chemical composition on the surface of the 1 wt% catalyst would be similar. Furthermore, H2-TPR measurements described in section 3.2.1.4 above also support the presence of Pd(0) as the only or predominant species on the surface.
Figure 3-9. XPS narrow scan of the Pd 3d region of a fresh sample of 10 wt% Pd/MgO using Mg Kα excitation as X-ray source.

Figure 3-10. XPS narrow scan of the Pd 3d region of a fresh sample of 5 wt% Pd/MgO using Mg Kα excitation as X-ray source.
3.2.1.6. XRD results

In order to further identify the crystalline phase of Pd in the catalyst, powder X-ray diffraction patterns of the three solids with different metal loadings were obtained, as shown in Figure 3-11. The Pd diffraction pattern of the 1 wt% Pd/MgO material was essentially undetectable because of the very low metal loading combined with a small particle size; all five peaks are assigned to MgO phase. When the metal loading is increased to 5 wt%, a small diffuse peak around $2\theta = 40^\circ$ starts to appear, which corresponds to the Pd (111) crystalline plane; the rest of the diffraction pattern is still indistinguishable from that of MgO. However, samples of the analogous 10 wt% Pd/MgO displayed clearer peaks associated with highly dispersed face centered cubic (fcc) crystalline Pd at $2\theta$ values of 40.3°, 46.8° and 68.3°, assigned to the (111), (200) and (220) planes, respectively. These values are consistent with those in the standard diffractogram of Pd (40.1°, 46.7° and 68.1°).[52] The most intense peak at $2\theta = 43.0$ ° is MgO (200),[53] which was used as an internal standard to assign the other signals. The fact that the diffraction peaks are difficult to detect is not unexpected, since the crystallinity is only associated with very small particles (as measured by TEM) that normally give rise to very diffuse peaks.

![Figure 3-11. Powder x-ray diffraction pattern 1, 5 and 10 wt% Pd/MgO.](image-url)
3.2.2. Catalytic hydrogenation

The catalytic properties of the new materials described in the preceding section were tested for the hydrogenation of a variety of N-heteroaromatic compounds representative of those commonly found in fossil fuels feedstocks; of alkene components of naptha (crude gasoline), and of biodiesel. The reaction conditions were optimized by systematically varying the operating temperatures and pressures. To determine the catalytic activity, the turnover frequency (TOF) was computed using:

\[
\text{moles of } H_2 \text{ consumed} / \text{moles of Ru} \times \text{time} \quad \text{(eq. 1)}
\]

The moles of H\(_2\) (\(n_{H_2}\)) consumed were in turn calculated from the change in H\(_2\) pressure (\(\Delta P\)) using the ideal gas law:

\[
\Delta P_{H_2} V_{H_2} = n_{H_2} R T_{H_2} \quad \text{(eq. 2)}
\]

Where, \(\Delta P_{H_2}\) is the change in gas pressure, \(V_{H_2}\) is volume of the gas based on the reactor volume (0.075 L) minus the liquid added, R is the gas constant (0.08206 L-atm/K-mol), and \(T_{H_2}\) is the temperature at which the reaction takes place. The slope (\(\Delta P/t\)) of the linear plot (Figure 3-12, right) was used to determine the moles of H\(_2\) consumed over time. Average TOF values were obtained from at least three independent experiments.

3.2.2.1. Hydrogenation of quinolines

The 1 wt% Pd/MgO catalyst is efficient and highly selective for the specific hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline (\(^{1}\)THQ) under moderate reaction conditions (150 °C and 40 atm H\(_2\)) using THF or hexane as the solvent. The progress of the reaction was followed by gas chromatography-mass spectrometry (GC-MS). A typical reaction profile is depicted in Figure 3-12 (left); the conversion reaches 100% after a few hours. The carbocyclic ring of quinoline is not hydrogenated to any detectable extent under these conditions.
The linear hydrogen uptake observed (Figure 3-12, right) during the first 1.5-2 h of the reaction (Figure 3-12, right) was used to calculate an initial turnover frequency (TOF$_{\text{init}}$) of $300 \pm 10 \text{ h}^{-1}$. This value was subsequently corrected for metal dispersion to yield a TOF$_{\text{corr}}$ of $6400 \pm 200 \text{ h}^{-1}$.

The influence of pressure and temperature on the hydrogenation of quinoline was evaluated using 1 wt% Pd/MgO. As shown in Figure 3-13 (left), TOF$_{\text{corr}}$ values increase steadily with H$_2$ pressure within the range 20-40 atm, indicating that the catalyst does not undergo metal sintering or any other deactivating processes to a significant extent at H$_2$ pressures of up to 40 atm, in agreement with our TEM observations (Figure 3-5). Moreover, the catalytic activity also increased with the temperature in a typical manner between 100-150 °C, as depicted in Figure 3-13 (right), indicating that the material is also thermally stable within that temperature range. Although it is likely that hydrogenation rates can be further increased by using higher pressures and temperatures, we consider the balance between the TOF values obtained and the mild
conditions employed satisfactory.

Figure 3-13. Hydrogenation of quinoline over 1 wt% Pd/MgO (\(n_{sub} : n_{Pd} = 1000\) in THF). Left: Influence of pressure on hydrogenation rate, 150 °C; Right: Effect of temperature on hydrogenation rate at 40 atm.

For comparison, commercial 5% Pd/SiO\(_2\) and 5% Pd/Al\(_2\)O\(_3\) catalysts were used to hydrogenate quinoline to \(^1\)THQ at 150 °C and 40 atm H\(_2\). As depicted in Figure 3-14, 5% Pd/SiO\(_2\) and 5% Pd/Al\(_2\)O\(_3\) catalysts displayed activities about four times lower than that of our 1 wt% Pd/MgO under analogous reaction conditions and equivalent amounts of Pd, yielding TOF\(_{corr}\) values of 1600 h\(^{-1}\) and 1500 h\(^{-1}\), respectively. To our knowledge, only one other quinoline hydrogenation catalyst containing Pd NPs (supported on hyperbranched aramids) is known.\(^{[54]}\) In that case, uncorrected TOF values of ~350 h\(^{-1}\), comparable to ours, were achieved.
Figure 3-14. Comparison of 1 wt% Pd/MgO with commercial catalysts for hydrogenation of quinoline to $^1$THQ at 150 °C and 40 atm H$_2$; $n_{sub}$ : $n_{Pd} = 1000$ hexane.

The 1 wt% Pd/MgO catalyst is also efficient and highly selective for the hydrogenation of methyl-substituted quinolines under analogous reaction conditions, as summarized in Table 3-2. Introduction of a methyl group in the 2-, 3-, and 8-position of quinoline results in lower hydrogenation rates. All the substrates were exclusively hydrogenated at the heterocycle with no evidence for products of the hydrogenation of the carbocycle being observed in any experiment. The introduction of a methyl group in quinoline results in a moderate decrease in TOF, but the position of substitution does not appear to have a marked effect on the hydrogenation rate. This may be interpreted as essentially a steric effect of the methyl group, making the approach of the planar substrate to the catalyst surface less efficient, but the available data is not sufficient to arrive at a definite conclusion on this point. We are not aware of any reported example of the hydrogenation of substituted quinolines using palladium.
Table 3-2. Hydrogenation of quinolines over 1 wt% Pd/MgO

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>TOF (h⁻¹)</th>
<th>TOF corr (h⁻¹)</th>
<th>Product and % conversion after 2h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>![Substrate Image]</td>
<td>300 ± 10</td>
<td>6400 ± 200</td>
<td>![Product Image] 100 %</td>
</tr>
<tr>
<td>2</td>
<td>![Substrate Image]</td>
<td>280 ± 1</td>
<td>5900 ± 20</td>
<td>![Product Image] 91 %</td>
</tr>
<tr>
<td>33</td>
<td>![Substrate Image]</td>
<td>250 ± 5</td>
<td>5300 ± 60</td>
<td>![Product Image] 87 %</td>
</tr>
<tr>
<td>4</td>
<td>![Substrate Image]</td>
<td>250 ± 30</td>
<td>5400 ± 600</td>
<td>![Product Image] 58 %</td>
</tr>
</tbody>
</table>

* In n-hexane; n_{sub} : n_{Pd} = 1000; 150 °C, 40 atm H₂.

3.2.2.2. Hydrogenation of alkenes

We were also interested in studying the catalytic activity of 1 wt% Pd/MgO for the hydrogenation of olefins in the context of improving the properties of crude gasoline (naphtha). Fluid catalytic cracking (FCC) naptha from refineries contains up to 40 % (C5-C6) alkenes, while the final product (gasoline) must have no more than 12 %. This step, crucial to avoid polymerization and wax formation during combustion, is generally achieved by hydrogenation during hydrodesulfurization (HDS). However, since branched and highly substituted alkenes are responsible for high octane rating, it is important to only hydrogenate the linear unsubstituted alkenes in this process.\[^{[55]}\]
We thus examined the catalytic activity of 1 wt% Pd/MgO under mild conditions (10 atm and 25 °C) for the hydrogenation of C5-C6 olefins representative of naphtha components, with different degrees of substitution at the C=C bond (see Table 3-3). We observed that our 1 wt% Pd/MgO catalyst is highly selective towards hydrogenating unsubstituted olefins, reaching TOFcorr values of up to 60,000 h⁻¹ for 1-hexene. The activity decreases sharply with increasing congestion around the double bond. Previous reports of C6-alkene hydrogenation using Pd NPs supported on silica indicated TOF values ranging from 4000-38000 h⁻¹ under similar reaction conditions.⁵⁶

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>TOF (h⁻¹)</th>
<th>TOFcorr (h⁻¹)</th>
<th>Product at 2h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>2300 ± 200</td>
<td>5000 ± 4600</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>2800 ± 50</td>
<td>6000 ± 1000</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>180 ± 20</td>
<td>3800 ± 470</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>90 ± 10</td>
<td>1900 ± 170</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>70 ± 1</td>
<td>1500 ± 15</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>1800 ± 450</td>
<td>39000 ± 9600</td>
<td></td>
</tr>
</tbody>
</table>

ₐₙₕₐₜ : nPd = 1000; RT, 10 atm H₂.
3.2.2.3. Partial hydrogenation of biodiesel

Since our 1 wt% Pd/MgO catalyst proved to be very active for the mild hydrogenation of 1-undecene (Table 3-3, entry 6), it seemed interesting to evaluate its efficacy in the partial hydrogenation of a biodiesel prepared by transesterification of soybean oil with methanol using KOH as the catalyst. The composition of the biodiesel, determined by GC-MS, is shown in Fig. 3-15 (left), where in \( C_n : x \), \( n \) indicates the number of carbons and \( x \) the number of \( \text{C}=\text{C} \) bonds in the fatty acid methyl esters (FAMEs). We found that about 50% of the biodiesel consisted of 18 carbon long chains with up to three \( \text{C}=\text{C} \) bonds (C18:3). Our goal was to partially hydrogenate the polyunsaturated (C18:3 and C18:2) esters to monounsaturated (C18:1) ester, without increasing the proportion of the fully saturated components (C18:0 and C16:0, initially 14%).

After preliminary screening for optimal reaction conditions in the range 25-100 °C/1–7 atm \( \text{H}_2 \), we were able to rapidly and selectively convert the mixture of FAMEs into predominantly (> 80%) the desired C18:1 product, under extremely mild conditions (100 °C and 1 atm \( \text{H}_2 \)) (Figure 3-15, right). No further reduction to the fully saturated species was observed even at longer reaction times. The final composition achieved corresponds to an upgraded first-generation biodiesel with improved stability and performance, indicating that our 1 wt% Pd/MgO catalyst could be of practical use in this type of application.
3.2.3. Catalyst recyclability

Additional experiments were performed to determine the recyclability and stability of the catalyst over three consecutive hydrogenation runs using the same sample of 1 wt% Pd/MgO, for cyclohexene and for quinoline. Figure 3-16 shows the corrected TOF values for each hydrogenation cycle, together with the normalized hydrogenation activities. The hydrogenation activities for cyclohexene displayed about ± 10% variation, which is on the order of the experimental error of our TOF measurements, suggesting the catalyst is stable and reusable for alkene hydrogenation for at least three cycles without significant loss of catalytic activity.

In contrast, recycling the catalyst in quinoline hydrogenation reactions resulted in about 30% loss of activity after the third run. Likewise, commercial 5% Pd/SiO₂ and 5% Pd/Al₂O₃ catalysts experience similar loss of activity during quinoline hydrogenation recycling under the same conditions.

**Figure 3-15.** GC/MS analysis of the composition of crude biodiesel and hydrogenated biodiesel before (left) and after (right) hydrogenation over Pd/MgO at 100 °C and 1 atm H₂.
In an effort to explain the origin of the loss of activity during quinoline hydrogenation, the following further tests were conducted:

(I) ICP-AES analysis of the catalyst recovered from quinoline recycling experiments revealed essentially no loss of Pd from the catalyst, while the liquid organic phase contained only trace amounts of Pd. Therefore, the observed loss of activity cannot be ascribed to leaching of the metal into the solution.

(II) TEM analysis of a used catalyst (Figure 3-7) showed no significant aggregation into larger Pd NPs that could account for a decrease in the catalytic efficiency was observed.

(III) The rate of hydrogenation of a 50:50 quinoline/1,2,3,4-tetrahydroquinoline mixture was very similar to that of quinoline alone, which rules out the possibility of inhibition by the product 1,2,3,4-tetrahydroquinoline. Based on these analyses, and the fact that no such deactivation effect is observed during alkene hydrogenation, it is concluded that the observed moderate decrease in activity is likely due to the presence of an unidentified trace impurity in quinoline, which accumulates after several catalytic cycles.
3.3. **Conclusions**

We have synthesized a new catalyst composed of Pd nanoparticles supported on MgO. TEM measurements reveal well-dispersed Pd particles of about $1.7 \pm 0.6$ nm. The catalyst was further characterized by XPS, XRD, hydrogen pulse chemisorption and H$_2$-TPR measurements. The new material was efficient for the regioselective hydrogenation of the heterocyclic ring of quinolines under moderate reaction conditions (150 ºC, 40 atm H$_2$), as well as for the mild reduction (25 ºC and 10 atm H$_2$) of a variety of alkenes representative of fuel components, and the partial saturation of biodiesel under atmospheric hydrogen pressure at 100 ºC. The catalyst was about four times more active in the hydrogenation of quinoline than commercial Pd/SiO$_2$ and Pd/Al$_2$O$_3$ catalysts, and it was recyclable for alkene hydrogenation for at least three cycles without significant loss of catalytic activity, while a 30% loss of activity was observed after three catalytic runs of quinoline hydrogenation, probably due to inhibition by trace impurities in the substrate.

3.4. **Experimental**

3.4.1. **Materials**

Na$_2$PdCl$_4$ (Pressure Chemicals, Inc.), 5% Pd/SiO$_2$ and 5% Pd/Al$_2$O$_3$ (Strem Chemicals) were used as received. Solvents (analytical grade, Sigma-Aldrich) were purified using a PureSolv purification unit from Innovative Technology, Inc. and further deoxygenated with a nitrogen flow prior to use. Substrates and other reagents (Sigma-Aldrich) were purified by appropriate methods prior to use as necessary. Magnesium oxide (~325 mesh, ≥ 99% trace metals basis) (Sigma-Aldrich) was calcined prior to metal loading at 500 ºC in the air for 2 h. Biodiesel was synthesized by a standard procedure: in short, a sonicated solution of KOH (0.875 g) in methanol
(50 cm$^3$) was added to commercial soybean oil (250 cm$^3$) and the mixture was stirred at 60 °C for 75 min. The biodiesel phase was separated and then heated to 80 °C for 15 min to remove residual methanol. The product was washed six times with warm water to remove glycerol and remaining KOH, then heated to 110 °C for 20 min and finally dried over sodium sulfate overnight.

3.4.2. Synthesis of Pd/MgO

To prepare the 1 wt% Pd/MgO catalyst, magnesium oxide (2.0 g) was placed in a 3-neck round bottom flask under nitrogen. Dry deoxygenated methanol (10 cm$^3$) was added and the mixture was stirred. Two pressure-equalizing dropping funnels were attached to the flask, one containing Na$_2$PdCl$_4$ (0.055 g; 0.02 g Pd; 0.188 mmol) in dry deoxygenated methanol (10 cm$^3$) and the second containing NaBH$_4$ (0.142 g; 3.76 mmol) in the same solvent (20 cm$^3$). Approximately 10 cm$^3$ of the borohydride solution was added quickly to the flask and the mixture was stirred for a few minutes. Subsequently, both the Na$_2$PdCl$_4$ and the remaining NaBH$_4$ solutions were added simultaneously to the flask at the rate of about one drop per second. After the addition was complete, the dark gray solution was stirred for 4 h under nitrogen at room temperature. The product was filtered under nitrogen, washed three times with methanol (10 cm$^3$), and dried under vacuum at room temperature overnight. Analysis by ICP-AES (Micro-Analysis, Inc., Wilmington) confirmed a metal content of 0.9 wt%. Materials containing 5 wt% and 10 wt% Pd/MgO were prepared by use of the same procedure, adjusting the amount of Na$_2$PdCl$_4$ to 0.275 g (0.10 g, 0.94 mmol Pd) and 0.550 g (0.20 g, 1.88 mmol Pd), respectively, and NaBH$_4$ to 0.711 g (18.8 mmol) and 1.42 g (37.56 mmol), respectively. The metal content was verified by ICP-AES analysis in both cases as 4.4 % and 9.7 %, respectively.
3.4.3. TEM studies

Transmission electron microscopy analysis was conducted at the Environmental Sciences Analytical Center (ESAC) of the Earth and Environmental Sciences Department of Brooklyn College using a JEOL TEM-2010 high-resolution microscope, operating at an accelerating voltage of 200 kV and providing point-to-point resolution of 0.19 nm. Samples for analysis were prepared by placing a drop of a suspension of the catalyst in hexane on a copper grid and allowing it to air-dry. Images were captured using an AMT camera system.

3.4.4. XRD measurements

Powder x-ray diffraction (XRD) patterns were obtained at the Environmental Sciences Analytical Center (ESAC) of the Earth and Environmental Sciences Department of Brooklyn College on a Phillips X’PERT MPD diffractometer, using monochromatic Cu-Kα radiation at 45 kV and 40 mA and 2θ scanning from 20° to 90°. Samples were ground in a mortar prior to analysis in the air at room temperature.

3.4.5. XPS measurements

XPS spectra were recorded using an Omicron XPS spectrometer equipped with a multichannel hemispherical analyzer and a dual Al/Mg X-ray source using Mg Kα excitation (1253.6 eV) performed at the College of Staten Island. The powdered sample was mounted on studs using a double-sided adhesive tape in air. The data analysis was performed by deconvoluting the XPS peaks by curve fitting using XPSPEAKS 4.1, applying Shirley background subtraction and Lorentzian-Gaussian functions (20% L, 80% G). The charging effect was corrected based on the literature value of 529.9 eV for the O 1s peak in MgO.\textsuperscript{[57]} \textsuperscript{[58]}
3.4.6. Hydrogen pulse chemisorption

Chemisorption measurements were performed using a Micromeritics ChemiSorb 2750 instrument, coupled to a TPx system controller. The fresh catalyst was reduced in 10% H\textsubscript{2}/Ar at 150 °C for 30 min and then purged with Ar at 150 °C for 30 min to remove impurities; after which the sample was allowed to cool to room temperature. Doses of 10% H\textsubscript{2}/Ar were repeatedly introduced to the sample tube until no further H\textsubscript{2} uptake was observed. The gas composition was analyzed by use of TCD detector. The metal dispersion was determined by built-in software that detects the amount of hydrogen adsorbed for each atom of palladium, using a 1:1 H:Pd model.\textsuperscript{[57]}

3.4.7. H\textsubscript{2}-TPR analysis

Temperature programmed reduction (TPR) of catalyst samples was also conducted in the Chemisorb 2750 instrument equipped with a thermal conductivity detector (TCD). About 120 mg of sample was first degassed at 200 °C in a flow of Ar gas (25 mL/min) for 1 h and then cooled down to room temperature. The carrier gas was then switched to a 9.9% H\textsubscript{2}/Ar gas mixture; after 10 min when the baseline of the TCD signals was stable, the sample was heated linearly at a rate of 10 °/min to 700K. The TCD signal change was displayed in real time on the computer interfaced to the instrument through the TPx system.

3.4.8. Catalytic tests

3.4.8.1. Hydrogenation of quinolines

Hydrogenation of quinolines was carried out in a glass-lined 5500 Parr reactor (100 cm\textsuperscript{3}) equipped with an internal stirrer, a thermocouple, a dip tube and a sampling valve, coupled to a 4843 controller and a Ashcroft Instrument pressure gauge for hydrogen monitoring. Typically the reactor was loaded with the catalyst (100 mg) and the desired amount of substrate in 30 cm\textsuperscript{3}
of solvent. The reaction mixture was deoxygenated by flushing with H₂ (20 atm) three times. The reactor was pressurized with H₂ at room temperature to 33 atm and then heated while stirring until the temperature reached 150 °C; at that point the pressure was adjusted to 40 atm and this was taken as the zero time for each reaction. The progress of the reaction was followed by monitoring the H₂ uptake. At the end of the run, a sample of the final mixture was analyzed by GC-MS using a Varian 3900 gas chromatograph fitted with a FactorFour VF-5ms capillary column and a Saturn 2100T mass detector. TOFᵢₙᵢₜ values were calculated from the slope of the linear part of TON vs. t plots. Average TOF values were obtained from at least three independent experiments. Finally, TOF values were corrected for metal dispersion (TOF₉₀), using the data obtained from chemisorption.

### 3.4.8.2. Hydrogenation of alkenes

Experiments were carried out using a 5000 Parr multireactor (75 cm³) equipped with a magnetic stirrer and a thermocouple, and coupled to a 4871 controller. The reactor was loaded with the catalyst (100 mg) and the substrate (10 cm³), flushed with H₂ (5 atm) three times, and then pressurized to 10 atm H₂ at room temperature. Stirring was initiated at that point, which was taken as the zero time for the reaction. At the end of the run, a sample of the mixture was analyzed by use of a Shimadzu 2010 gas chromatograph fitted with an FID detector and an Agilent HP-Al/S capillary column. Each experiment was repeated at least three times in order to ensure reproducibility.

### 3.4.8.3. Partial hydrogenation of biodiesel

Partial hydrogenation of biodiesel was carried out in a low-pressure 5100 Parr glass reactor (160 cm³) equipped with a thermocouple and a stirrer, and coupled with a 4848 controller. The reactor was loaded with the catalyst (100 mg) and the biodiesel (75 cm³), and flushed three times with 1
atm H₂. The mixture was heated while stirring until the desired temperature was reached, which was taken as zero time for the reaction. The mixture was kept under a constant H₂ pressure of 1 atm and the hydrogenation progress was followed by taking samples every 10 min and immediately analyzing them by GC-MS on a Supelco SP-2330 capillary column.

### 3.4.8.4. Recycling experiments

A quinoline hydrogenation run was performed as described in section 3.4.8.1, using 1 mL of quinoline and 30 cm³ hexane as the solvent. At the end of reaction, the reactor was cooled to room temperature and the catalyst was allowed to settle down; the supernatant liquid was carefully withdrawn as much as possible and 1 mL of fresh quinoline and 30 cm³ of solvent were added. A second hydrogenation run was then started following the same procedure; further recycling steps were carried out by repeating the same procedure.

When using cyclohexene as the substrate, 10 mL of neat cyclohexene was used in the first run and the experiments were carried out at room temperature. After 3 h of reaction, another 10 mL of fresh cyclohexene was added and a second run was started. The hydrogenation was carried out for three runs in total.
Chapter 4

Hydrogenation of N- and S-heteroaromatic and aromatic compounds and dehydrogenation of N-heterocycles by ruthenium nanoparticles immobilized on pyridine-functionalized carbon nanotubes

4.1. Introduction

4.1.1. New catalytic system for hydrogenation of heteroaromatic and aromatic compounds

In our previous work described in the preceding chapter, we discovered a Pd/MgO catalyst that is active in the selective hydrogenation of the heterocyclic ring of quinolines, of linear and unsubstituted alkenes, and of excessive unsaturations in fatty acid methyl esters (FAMEs). Although this selectivity is interesting and may be exploited in specific applications, we noted that our Pd system was not active in the hydrogenation of S-heteroaromatic, or plain aromatic compounds, which is within our wider interest in reactions of relevance to fossil fuel upgrading. In search of more active and versatile catalysts, we decided to switch to ruthenium, which has been generally found to be more active than Pd for highly demanding aromatic hydrogenation reactions. Moreover, in a similar work performed by Dr. M. Fang in our laboratory, a catalyst containing ruthenium nanoparticles immobilized on magnesium oxide (Ru/MgO) was highly successful in hydrogenating a wide variety of N- and S-heteroaromatic and aromatic compounds.
With the Pd/MgO catalyst, we observed that due to the highly porous nature of magnesium oxide, though extremely small (1.7 ± 0.6 nm), most of the metal particles were located on the support in places where they were unavailable for any catalytic activity. As a result, only 4.7 % of the total metal loaded (1 wt%) was taking part in catalysis. With this knowledge, we set out to search for alternative solid supports with basic functionalities, with larger specific surface area than MgO (88 m² g⁻¹) and lower porosity, and that would be stable under strong reaction conditions (high temperatures and pressures). For such purposes, carbon nanotubes (CNTs) are highly attractive; they are known for their high specific surface area (maximum value measured 1050 m²/g), versatility, thermal and chemical stability, and for their unique electronic, mechanical and structural properties.[61]

The use of carbon nanotubes as support for ruthenium nanoparticles has been reported for some assortment of hydrogenation reactions (e.g. arenes,[62] phenylacetylene,[63] cinnamaldehyde,[64] and cellulose[65]). Moreover, some studies have demonstrated that CNTs promote higher activity than when other carbon (e.g. activated carbon) and non-carbon materials (e.g. Al₂O₃, TiO₂, MgO, and ZrO₂) supports are used.[61a, 66] No examples of Ru nanoparticles on carbon nanotubes for N- and S-heteroaromatic hydrogenation were found.

4.1.2. Dehydrogenation of organic liquid for hydrogen storage applications

As mentioned in the General Introduction Chapter, hydrogen is the most promising proxy as an energy carrier due to its high abundance in the universe, and its ability to burn without forming any noxious gases,[27] besides having the largest energy content per kilogram compared to all other fuels.[28a] At present, most of the hydrogen is produced from fossil substances and a great deal of research is currently devoted to discover efficient ways of producing H₂ from water. Besides the need for efficient methods for producing hydrogen, a critical issue that needs to be
addressed before a hydrogen-based energy structure can be put in place is a safe and effective way of storing and transporting large amounts of hydrogen. Although much effort has been devoted to the development of solid hydrogen storage materials, much improvement is needed before they can be widely applied. In contrast, storage, and transport of liquids are commonplace in industry, and this could make liquid H₂ storage materials preferable to solids.[29] The vast infrastructure of the oil and petrochemical industries (150,000 miles of pipes and over 100,000 gas stations in the US alone) could be adapted for H₂-storage liquids. Also, vehicles possessing a liquid fuel tank are accepted as safe and efficacious.

Several classes of organic liquids have been proposed as H₂ storage materials: hydrocarbons, such as, decalin and cyclohexane have a high hydrogen storage capacity, although they are not practical since their dehydrogenation to the corresponding aromatics is endothermic. Hrein Energy Inc. is commercializing such a process in Japan and Europe.[28b] N-heteroaromatic compounds on the other hand, can release H₂ at mild conditions. For example, it has been reported that 9-ethylcarbazole releases hydrogen at 150–200 °C.[67] However, since it is solid below 60 °C, transportation of used material is a challenge underlining the need to discover other organic compounds that may be used to store and release hydrogen at mild conditions.

4.2. Results and discussion

4.2.1. Catalyst preparation and characterization

4.2.1.1. Ruthenium nanoparticles on acid-oxidized carbon nanotubes (Ru/AO-CNTs)

Prior to the work described in this thesis, a first material, based on Ru nanoparticles supported on carbon nanotubes was synthesized by other members of our group (Dr. A. Sánchez, post-doc, and D. Vovchok, undergraduate). Due to the inert nature of pristine CNTs, they were first treated
with strong acid (HNO₃/HCl) solution; acid oxidation introduces surface functional groups, such as carboxylic (–COOH), hydroxyl (–OH), and carbonyl (–CO) that improve the metal deposition.⁶⁸ In addition, it has been reported that the functionalization of carbon materials with nitrogen, oxygen, and other groups increases the catalytic activity of the materials under mild reaction conditions.⁶⁹ The acid (HNO₃/HCl) oxidized carbon nanotubes (AO-CNTs) were used to deposit ruthenium nanoparticles using the NaBH₄ reduction method in methanol, and the resulting Ru/AO-CNTs were characterized using TEM and XPS (Figure 4-1). Some preliminary experiments indicated a good catalytic potential in the hydrogenation of aromatics, and therefore, we re-synthesized this material and employed it as a starting point for the research described in this Chapter.

![Figure 4-1. TEM micrograph (left), and Ru 3p XPS spectra (right) of fresh 5 wt% Ru/AO-CNTs.](image)

### 4.2.1.2. Synthesis and characterization of pyridine functionalized carbon nanotubes (py-CNT)

Since one of our aims was the activation of hydrogen through heterolytic mechanisms, we decided to modify the carbon nanotubes, in order to obtain a functional catalyst support and
enhance the catalytic efficiency. It has been previously shown by our group that the presence of pyridine groups adjacent to metal sites in a catalyst composed of ruthenium nanoparticles supported on poly(4-vinylpyridine) (Ru/PVPy) results in high activity for the hydrogenation of a variety of aromatic compounds, following an ionic pathway in the case of N-heterocycles, as shown in Figure 4-2.[70] Through this mechanism, the substrate does not bind directly to the metal. Instead, the hydrogenation occurs through an outer sphere transfer of the proton from the surface pyridinium group and a hydride attached to the metal. Employing this concept, we set out to functionalize the carbon nanotubes by introducing pyridine groups, with the aim of creating bi-functional nanostructures composed of the metal particle in close association with the basic pyridine sites on the surface.

![Figure 4-2](image)

**Figure 4-2.** Heterolytic splitting of H₂ and ionic hydrogen transfer to polar bonds, assisted by the basic sites of the support on Ru/PVPy catalyst.[70]

The desired material, consisting of ruthenium nanoparticles supported on pyridine-functionalized multiwalled carbon nanotubes, was prepared according to the overall procedure shown in Scheme 4-1. The tubes were first modified with pyridine, followed by the deposition of ruthenium nanoparticles produced by a chemical reduction method.
The purified multiwalled carbon nanotubes (MWNTs) (discussed in detail in the Experimental section) were functionalized with pyridine groups using a known method. In this reaction, treatment of 4-aminopyridine with a strong oxidizing agent (NaNO₂) in 4 M HCl solution results in the formation of pyridinium diazonium salt, as shown in Scheme 4-2.

Scheme 4-1. Overall scheme of carbon nanotubes functionalization followed by metal deposition.

Scheme 4-2. Functionalization of carbon nanotubes with pyridine groups using 4-aminopyridine and sodium nitrite in hydrochloric acid.

The addition of HCl to the aminopyridine is crucial to ensure the protection of the pyridine nitrogen through protonation to prevent oxidation by the nitrite. The MWNTs donate an electron to the diazonium salt and yield a CNT-radical cation and an aryl radical. These highly active aryl radical species then add to the carbon nanotubes and form a covalent bond. At the end of the
reaction, the carbon nanotubes are treated with sodium hydroxide to deprotonate the pyridinium salt. The resulting pyridine-functionalized carbon nanotubes are then isolated and dried overnight under vacuum.

The presence of pyridine functional group on the carbon nanotubes was confirmed by x-ray photoelectron (XPS) analysis of the purified CNTs before and after the functionalization. The XPS spectrum of purified carbon nanotubes shows the presence of O 1s (530 eV) and C 1s (284.5 eV) peaks only, as shown in Figure 4-3 (top). Moreover, carbon nanotubes are confirmed in this way to be free of any nitrogen species (399 eV). After the functionalization of carbon nanotubes with pyridine groups, a strong peak appears at 399 eV, characteristic of N 1s binding energy, see Figure 4-3 (bottom).
4.2.1.3. Synthesis of 5 wt% Ru/py-CNTs

The catalyst was prepared via deposition precipitation method. Through this process, metals, metal oxides, metal hydroxides, and metal sulfides can be deposited onto the surfaces of supports. The soluble metal precursor is precipitated out through a chemical reaction, generally using a reducing agent, e.g. NaBH₄,¹⁶b or hydrazine,⁷³ followed by deposition of the metal species onto the solid support present in the reaction vessel. This method is advantageous in the case of organic supports, since room temperatures are sufficient to propel the reaction forward. Employing this method, the 5 wt% Ru/py-CNTs catalyst was synthesized by reducing RuCl₃.3H₂O with excess NaBH₄ in methanol at room temperature in the presence of pyridine functionalized carbon nanotubes, as shown in Scheme 4-3.⁷¹

Figure 4-3. XPS survey scans of CNTs (top), and narrow scan in the N 1s region of py-CNTs (bottom).
Scheme 4-3. Ruthenium metal deposition on pyridine functionalized carbon nanotubes using sodium borohydride.

Upon completion, the pale brown solution became colorless; after appropriate work up (described in detail in the Experimental Section) the dark solid was stored under inert atmosphere. This method of catalyst preparation is highly reproducible, and leads to well dispersed metal particles over the carbon support. In addition, after washing the catalyst was free of any counter-ions. Moreover, the catalyst remained predominantly stable even after multiple, short exposures to air during sample retrievals.

4.2.1.4. TEM measurements of 5 wt% Ru/py-CNTs

Since smaller particle size leads to a larger surface area\[^{74}\] that can result in more active site for catalysis, we had aimed to synthesize nano-sized particles. To determine the outcome of our synthetic method and measure the size of the ruthenium particles, transmission electron microscope (TEM) was employed. As depicted in Figure 4-4, the ruthenium nanoparticles immobilized on carbon nanotubes are uniform and well dispersed with an average diameter of 1.7 ± 0.4 nm, calculated by measuring >490 randomly chosen particles from several micrographs.

Additionally, it is difficult to conclude whether the nanoparticles are located inside or outside the carbon nanotubes, solely based on the 2D TEM images of the catalyst surface. However, previous studies have shown that carbon nanotubes with an average diameter of up to 20-30 nm have metal nanoparticles deposited mainly on the outside of the tubes.\[^{66b}\] This trend is
attributed to the lack of ability of a liquid to enter the carbon nanotubes with a diameter of <20 nm, in a suspension. Since our commercially purchased multiwalled carbon nanotubes have an average diameter of 5-7 nm, it is safe to assume that the majority of the ruthenium metal particles are located on the outside of the nanotubes.

![Figure 4-4. Transmission electron micrographs and particle size distribution histogram of a fresh sample of 5 wt% Ru/py-CNTs.](image)

**4.2.1.5. XPS analysis**

X-ray photoelectron spectroscopy (XPS) was performed to determine the composition of ruthenium nanoparticles. In the full survey scans of the 5 wt% Ru/Py-CNTs, the O 1s, Ru 3p\textsubscript{1/2}, Ru 3p\textsubscript{3/2}, N 1s and C 1s peaks were observed at around 532.5 eV, 484.5 eV, 462.2 eV, 399 eV, and 284.5 eV, respectively (Figure 4-5). No peaks were observed around 188 eV (B 1s) and 270 eV (Cl 2s), indicating that the catalyst surface is clean of any starting materials.
The narrow scan spectra (Figure 4-6) within the Ru 3d region (280-284 eV) shows an overlapping of Ru(0) 3d5/2 (281.2 eV) and C 1s (283–290 eV) peaks. The C 1s peaks can be further de-convoluted to at least two types of carbon peaks: C=C and C–O peaks with binding energies of 284.5 and 286.3 eV, respectively, originating from pyridine functionalized carbon nanotubes support.\cite{58,75}

A narrow scan spectra within the Ru 3p (462–485 eV) region further confirms the presence and elucidates the nature of ruthenium particles. As shown in Figure 4-7, the peaks at 484.5 eV and 462.2 eV correspond to the binding energies of Ru 3p1/2 and Ru 3p3/2 of Ru(0), respectively; no other Ru species were observed. These results suggest that not only our method of catalyst synthesis successfully yields Ru(0) species, exclusively, but the catalyst is also stable after being exposed to air during sample preparation.
Figure 4-6. C 1s and Ru 3d XPS spectra of a fresh sample of 5 wt% Ru/py-CNTs.

Figure 4-7. Ru 3p\textsubscript{1/2} and Ru 3p\textsubscript{3/2} XPS spectra of a fresh sample of 5 wt% Ru/py-CNTs.
4.2.1.6. XRD results of 5 wt% Ru/py-CNTs

To further confirm the presence of metallic ruthenium nanoparticles on 5 wt% Ru/py-CNTs, powder x-ray diffraction was employed. The diffraction patterns of carbon nanotubes and Ru/py-CNTs (Figure 4-8) show peaks at $2\theta = 25.6^\circ$(002), $42.7^\circ$(100), and $77^\circ$(110) that correspond to the carbon nanotubes support.[76] However, due to the low metal loading (5 wt%) and the fine nature of Ru nanoparticles, as confirmed by TEM, only a broad, weak peak characteristic of crystalline Ru(0) was observed at $2\theta = 44^\circ$(101).[26, 77]

![Figure 4-8. X-ray diffraction pattern of (a) py-CNT, and (b) fresh 5 wt% Ru/Py-CNTs.](image)

4.2.2. Catalytic Tests

4.2.2.1. Hydrogenation of quinoline over Ru/AO-CNTs

The activity of the 5-wt % Ru/AO-CNTs (acid-treated non-functionalized nanotubes previously prepared in our lab) was measured in order to have a basis for comparison for our ruthenium
catalyst over pyridine-functionalized carbon nanotubes catalyst. The 5 wt% Ru/AO-CNTs catalyst is highly effective and selective for the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline at 150 °C and 40 atm H₂ and a [substrate]:[Ru] of 1000 displaying a TOF_{init} of 3600 ± 700 h⁻¹.

4.2.2.2. Hydrogenation of quinoline over 5wt% Ru/py-CNTs

The new catalyst containing 5 wt% ruthenium on pyridine-functionalized carbon nanotubes (Ru/py-CNTs) was found to hydrogenate quinoline exclusively to 1,2,3,4-tetrahydroquinoline (1THQ) (determined by GC-MS), under moderate reaction conditions (150 °C and 40 atm H₂) in the absence of any solvent. The progress of the reaction was followed by measuring the H₂ uptake; a typical pressure vs. time (P vs. t) graph is depicted in Figure 4-9 (left). The catalytic activity is expressed as initial turnover frequency (TOF_{init}), defined as moles of H₂ consumed per mol of metal per hour, and calculated from the linear hydrogen uptake observed during the initial stage of each reaction (see Figure 4-9, right).

![Figure 4-9.](image)

**Figure 4-9.** Hydrogenation of quinoline catalyzed by 5 wt% Ru/Py-CNTs (150 °C, 40 atm H₂; \( n_Q : n_{Ru} = 1000 \)): reaction profile, P vs. t graph (left); slope obtained from the linear section of the plot of P vs. t (right).
Based on the initial rate of hydrogen uptake the initial turnover frequency (TOF$_{\text{init}}$) for quinoline hydrogenation is $6000 \pm 800$ h$^{-1}$ as shown in Table 4-1. In addition to being exceptionally active, the Ru/Py-CNTs catalyst is also highly selective for the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline ($^{1}$THQ). Such high selectivity is indicative of an ionic mechanism for quinoline hydrogenation, as has been earlier proposed by us for the Pd/MgO, Ru/PVPy, and Ru/MgO catalysts (Scheme 4-4).$^{[70, 78]}$

![Scheme 4-4. Proposed mechanism for hydrogenation of quinoline by Pd/MgO, Ru/ PVPy, and Ru/MgO catalysts for the coordination of quinoline to the catalyst exclusively through $\equiv$N of the heterocycle, where B = base.]

Through this mechanism the quinoline probably interacts with the catalyst predominately through the N-heterocyclic ring, and as a result, no product of carbocyclic hydrogenation, 5,6,7,8-tetrahydroquinoline ($^{5}$THQ) is observed.$^{[79]}$ High selectivity towards $^{1}$THQ is also desirable due to its utility as a building block for agrochemicals, dyes, alkaloids, and pharmaceutically relevant products.$^{[80]}$

These results clearly support our hypothesis that the presence of basic sites neighboring the active metal sites enhances the catalytic activity, as the Ru/py-CNTs (TOF$_{\text{init}}$ 6000 h$^{-1}$) is
roughly two fold more active than the Ru/AO-CNTs (TOF_{init} 3600 h^{-1}) in the hydrogenation of quinoline at moderate reaction conditions.

**Table 4-1.** Hydrogenation of N-heteroaromatics over 5 wt% Ru/Py-CNTs\(^a\) after 2 h.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>TOF_{init} (h^{-1})</th>
<th>Products and % conversions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="Image" /></td>
<td>6000 ± 800</td>
<td><img src="image2" alt="Image" /> 99%</td>
</tr>
<tr>
<td>2</td>
<td><img src="image3" alt="Image" /></td>
<td>4900 ± 400</td>
<td><img src="image4" alt="Image" /> 70% <img src="image5" alt="Image" /> 16% <img src="image6" alt="Image" /> 6%</td>
</tr>
<tr>
<td>3</td>
<td><img src="image7" alt="Image" /></td>
<td>2100 ± 400</td>
<td><img src="image8" alt="Image" /> 26% <img src="image9" alt="Image" /> 8% <img src="image10" alt="Image" /> 30%</td>
</tr>
<tr>
<td>4</td>
<td><img src="image11" alt="Image" /></td>
<td>4900 ± 800</td>
<td><img src="image12" alt="Image" /> 75%</td>
</tr>
<tr>
<td>5</td>
<td><img src="image13" alt="Image" /></td>
<td>4700 ± 100</td>
<td><img src="image14" alt="Image" /> 69%</td>
</tr>
</tbody>
</table>

\(^a\) \(n_{\text{sub}} : n_{\text{Ru}} = 1000; 150^\circ \text{C}; 40 \text{ atm H}_2; \text{ solvent-free.}\)

Several other examples of metal-catalyzed quinoline hydrogenation have been reported in the literature with a wide range of activity under different reaction conditions. These include: Ru/SiO\(_2\),\(^{[21]}\) Ru–SiO\(_2@\)microporousSiO\(_2\),\(^{[81]}\) ruthenium nanoparticles over hydroxyapatite (HAP),\(^{[20]}\) ruthenium nanoparticles on polyorganophosphazenes (PDMP),\(^{[22]}\) Pd on mesoporous carbon graphitic nitrides (mpg-C\(_3\)N\(_4\)),\(^{[80b]}\) Rh nanoparticles on aluminum oxy-hydroxide
In these studies, the average turnover frequency was calculated based on the total number of moles of product per moles of metal over a set period of time (TOF_{avge}). For comparison, we also calculated our TOF_{avge} based on the moles of substrate converted for Ru/py-CNTs. Based on the comparison, summarized in Table 4-2, we found that despite the differences in reaction conditions, our catalyst system has by far the highest activity for the hydrogenation of quinoline to {^1}THQ. In particular, comparing our catalyst with Ru/HAP (50 atm and 150 °C) that has the similar reaction conditions, the Ru/py-CNTs catalyst is about 25 times higher in activity for the quinoline hydrogenation.

**Table 4-2.** Comparison of catalytic activities of different catalysts for the hydrogenation of quinoline.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>P (atm)</th>
<th>T (°C)</th>
<th>[Sub]:[M]</th>
<th>TOF_{avge} (h^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/py-CNTs</td>
<td>40</td>
<td>150</td>
<td>1000:1</td>
<td>2000</td>
</tr>
<tr>
<td>Ru/SiO_{2}^{[21]}</td>
<td>30</td>
<td>100</td>
<td>500:1</td>
<td>185</td>
</tr>
<tr>
<td>Ru/SiO_{2}@mSiO_{2}^{[81]}</td>
<td>30</td>
<td>80</td>
<td>150:1</td>
<td>30</td>
</tr>
<tr>
<td>Ru/HAP^{[20]}</td>
<td>50</td>
<td>150</td>
<td>150:1</td>
<td>85</td>
</tr>
<tr>
<td>Ru/PDMP^{[22]}</td>
<td>50</td>
<td>25</td>
<td>100:1</td>
<td>2</td>
</tr>
<tr>
<td>Pd@ompg-C_{3}N_{4}^{[80b]}</td>
<td>1</td>
<td>50</td>
<td>20:1</td>
<td>4</td>
</tr>
<tr>
<td>Rh/AIO(OH)^{[82]}</td>
<td>8</td>
<td>125</td>
<td>120:1</td>
<td>34</td>
</tr>
</tbody>
</table>

**4.2.2.3. Hydrogenation of other N-heteroaromatics**

In addition to quinoline, the Ru/py-CNTs catalyst was also tested for other N-heteroaromatic compounds, representative of components of fossil fuels, under moderate conditions (150°C and
40 atm). The 5 wt% Ru/py-CNTs was used to hydrogenate 2-methylquinoline (Table 4-1, entry 2). This substrate is more challenging to hydrogenate than quinoline on conventional catalysts due to the steric bulk of the methyl group in the C2 position, next to the N atom that must bind to the active metal site. Despite the steric hindrance, however, Ru/py-CNTs proves to be still highly active for the hydrogenation of 2-methylquinoline (TOF$_{\text{init}} = 4900 \pm 400$ h$^{-1}$) with 2-methyl-1,2,3,4-tetrahydroquinoline (2m$^{-1}$THQ) as the major product (70%). A smaller amount (16%) of 2-methyl-5,6,7,8-tetrahydroquinoline (2m$^{-5}$THQ) is also observed. The presence of 2m$^{-1}$THQ as the major product suggests that the substrate interacts with the catalyst predominantly through the N-heterocyclic ring and possibly through ionic pathways. Nevertheless, the appearance of 2m$^{-5}$THQ indicates that due to the steric hindrance caused by the alkyl group, 2-methylquinoline also interacts with the catalyst through the carbocyclic ring of the substrate, most likely via π interactions, resulting in low concentrations of 5-THQ product.$^{[21, 80b]}$ Other examples of 2-methylquinoline hydrogenation include Ru/HAP (TOF$_{\text{avege}} 50$ h$^{-1})^{[20]}$, Ru-SiO$_2$@mSiO$_2$ (TOF$_{\text{avege}} 150$ h$^{-1})^{[81]}$, Pd@mgp-C$_3$N$_4$ (TOF$_{\text{avege}} 4$ h$^{-1})^{[80b]}$ and Ir/CNTs (TOF$_{\text{avege}} 16500$ h$^{-1}$) performed at a wide range of reaction conditions.$^{[83]}$

Hydrogenation of indole (IN) (Table 4-1, entry 3) leads to a mixture of products, 1,2-dihydroindole (INE), 4,5,6,7-tetrahydroindole (THIN), and octahydroindole (OHIN) with TOF$_{\text{init}}$ of 2100 $\pm$ 400 h$^{-1}$ (TOF$_{\text{avege}} 320$ h$^{-1}$). In this case, the molecule is reacting with the catalyst efficiently through both the heterocycle and the carbocycle. This indicated that the ionic mechanism is not predominant, most likely due to the lower basicity of indole with respect to quinoline. Pyridine (Table 4-1, entry 4) was hydrogenated to piperidine with TOF$_{\text{init}}$ of 4900 $\pm$ 800 h$^{-1}$ (TOF$_{\text{avege}} 375$ h$^{-1}$), while pyrrole (Table 4-1, entry 5) was reduced to pyrrolidine with TOF$_{\text{init}}$ of 4700 $\pm$ 100 h$^{-1}$ (TOF$_{\text{avege}} 345$ h$^{-1}$). To the best of our knowledge, the only examples of
such versatility in the hydrogenation of N-heteroaromatics are those reported by our group for ruthenium nanoparticles supported on poly(4-vinlypyridine), Ru/PVPy,[70] and Ru/MgO,[78b] although with lower catalytic activities than 5 wt% Ru/py-CNTs.

4.2.2.4. Hydrogenation of S-heteroaromatics

The catalytic activity of 5 wt% Ru/py-CNTs was also evaluated in the hydrogenation of benzothiophene. Due to the highly poisoning nature of sulfur compounds over supported metal catalyst, they are immensely difficult to hydrogenate. For example, neither Ru/SiO$_2$ (100 °C and 30 atm),[79] nor a colloidal suspension of Rh (ambient conditions) is able to hydrogenate thiophene or benzothiophene,[84] despite their good activity towards N-heteroaromatic compounds. However, our 5 wt% Ru/py-CNTs catalyst is able to hydrogenate benzothiophene to 2,3-dihydrobenzothiophene (26 %) at 200 °C and 50 atm with a [substrate]:[M] ratio of 100 over 24 h in decahydropnaphthalene (confirmed by GC-MS), with a TOF$_{\text{avge}}$ of 1.1 h$^{-1}$, see Scheme 4-5. This activity is significantly higher than the previous work reported by our group using 10 wt% Ru/MgO (TOF$_{\text{avge}}$ 0.23 h$^{-1}$).[60] Although the activity achieved is still far from being of practical use, to the best of our knowledge this is the very first example of benzothiophene hydrogenation over a carbon nanotubes-supported ruthenium catalyst. This result validates our catalyst design and mechanistic model, and opens the way toward future developments of more active catalysts of possible practical utility in the very demanding hydrogenation of sulfur aromatics.

![Scheme 4-5. Hydrogenation of benzothiophene at 200 °C and 50 atm H$_2$ over 5 wt% Ru/py-CNTs](image_url)
4.2.2.5. Hydrogenation of arenes

The scope of substrates for our 5 wt% Ru/py-CNTs catalyst was further expanded by the hydrogenation of arenes, including toluene, \( p \)-xylene, and mesitylene at 150 °C, 40 atm and a [sub]:[Ru] of 1000 over 2h in the absence of solvent. The results of these tests are summarized in Table 4-3.

Hydrogenation of toluene (Table 4-3, entry 1) over 5 wt% Ru/py-CNTs yields methylcyclohexane, exclusively, with a \( \text{TOF}_{\text{init}} \) of 16000 h \(^{-1} \) (\( \text{TOF}_{\text{avg}} \) 3600 h \(^{-1} \)). No other (partially hydrogenated) products were observed by GC-MS, at the selected reaction conditions, as summarized in Table 4-4. Moreover, 5 wt % Ru/py-CNTs is also very active for the hydrogenation of \( p \)-xylene (Table 4-3, entry 2) and mesitylene (Table 4-3, entry 3), despite the steric hindrance introduced by the methyl groups, with \( \text{TOF}_{\text{init}} \) values of 10300 h \(^{-1} \) (\( \text{TOF}_{\text{avg}} \) 600 h \(^{-1} \)) and 1300 h \(^{-1} \) (\( \text{TOF}_{\text{avg}} \) 310 h \(^{-1} \)), respectively.

The catalytic activity of 5 wt% Ru/py-CNTs is significantly higher than those achieved in previous work by our group using ruthenium nanoparticles immobilized on basic supports Ru/PVPy and Ru/MgO with \( \text{TOF}_{\text{avg}} \) ranging from 69 – 1000 h \(^{-1} \).
Table 4-3. Hydrogenation of arenes over 5 wt% Ru/py-CNTs\textsuperscript{a} after 2 h.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>TOF\textsubscript{init} (h\textsuperscript{-1})</th>
<th>Products and % conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>🍒</td>
<td>16000</td>
<td>🍊 90%</td>
</tr>
<tr>
<td>2</td>
<td>🍒</td>
<td>10300</td>
<td>🍊 90%</td>
</tr>
<tr>
<td>3</td>
<td>🍒</td>
<td>1300</td>
<td>🍊 62%</td>
</tr>
</tbody>
</table>

\textsuperscript{a} n\textsubscript{sub} : n\textsubscript{Ru} = 1000; 150 °C; 40 atm H\textsubscript{2}; solvent-free.

Table 4-4. Comparison of catalytic activities of other ruthenium catalysts prepared by our group for the hydrogenation of substituted arenes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>P (atm)</th>
<th>T (°C)</th>
<th>[Sub]:[M]</th>
<th>TOF\textsubscript{avge} (h\textsuperscript{-1})</th>
<th>Toluene</th>
<th>p-Xylene</th>
<th>Mesitylene</th>
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<td>6</td>
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<tr>
<td>Ru/MgO\textsuperscript{[60]}</td>
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<td>120</td>
<td>1000:1</td>
<td>1000</td>
<td>—</td>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>
4.2.2.1.6. Catalyst recyclability test of 5wt% Ru/py-CNTs

The recyclability of 5 wt% Ru/py-CNTs was examined for three consecutive cycles of hydrogenation of neat quinoline at 150 °C and 40 atm H₂ over 2h at a [substrate]:[Ru] ratio of 1000. As shown in Figure 4-10, the catalyst displays a persistently high activity for up to three cycles. This suggests that the catalyst is highly stable and does not undergo any deactivation, or poisoning by the substrate or the products overtime.

Figure 4-10. Catalytic activity of 5 wt% Ru/py-CNTs during recycling experiments.

4.2.2.1.7. Possible hydrogenation mechanism

Although a full mechanistic study of our catalytic reactions was outside the scope of this dissertation, based on previous work by our group and on the hydrogenation results on 5 wt% Ru/py-CNTs for a variety of N-heteroaromatics (summarized in Table 4-1), some reasonable considerations concerning a possible hydrogenation mechanisms are presented below. It is expected that molecular hydrogen interacts with the catalyst through two distinct pathways: 1)
heterolytic hydrogen activation mechanism (path a) taking place at the perimeter of the nanoparticles in close proximity to the pyridine groups of the support (‘Type A’ site), and 2) homolytic hydrogen activation mechanism over the bulk of the nanoparticles (path b), away from basic sites of the support (‘Type B’ site) (Figure 4-11). Through the heterolytic mechanism, with the assistance from the basic functional groups adjacent to metal sites, the hydrogen molecule is cleaved into a hydride and a proton on ‘Type A’ sites. On the contrary, through homolytic hydrogen activation mechanism, on ‘Type B’ sites hydrogen molecule is dissociated into two hydrogen atoms on the metal surface, which may either transfer directly to the substrate during hydrogenation reaction, or possibly migrate and diffuse on the carbon surface, prior to being transferred to the substrate, in a phenomenon known as hydrogen spillover.\[31\]

![Figure 4-11. Possible hydrogen activation mechanisms on 5 wt% Ru/py-CNTs.](image)

As shown in Table 4-1, hydrogenation of quinoline over 5 wt% Ru/py-CNTs yields 1,2,3,4-tetrahydroquinoline, exclusively, at 150 °C and 40 atm H$_2$. It is expected that quinoline would first hydrogenate to 1,2-dihydroquinoline predominantly through a heterolytic mechanism at ‘Type A’ sites, where H$_2$ would split to H$^-$ and H$^+$ over ruthenium nanoparticles and basic pyridine sites, respectively. Due to the strongly basic nature of quinoline, it would be prone to
hydrogen-bond to the pyridinium site, thereby promoting the simultaneous outer-sphere transfer of the proton from the basic site of the support to the nitrogen atom of quinoline and the hydride from the metal center to the α-carbon atom, resulting in the formation of 1,2-dihydroquinoline. The 1,2-dihydroquinoline intermediate would then migrate to ‘Type B’ site, and get further reduced to 1,2,3,4-tetrahydroquinoline through hydrogenation of the non-polar C=C bond by the atomic hydrogen present on the active ruthenium metal sites. A possible mechanism and reaction intermediates is shown in Scheme 4-5, below. Simple arenes, such as toluene, are expected to undergo hydrogenation by hydrogen atom transfer taking place at ‘Type B’ sites, since in this case the possibility of hydrogen-bonding to pyridinium is not a driving force. On the other hand, hydrogenation of benzothiophene may be expected to occur either through hydrogen atom transfer at ‘Type B’ sites, as an alkene, or through heterolytic hydrogen activation mechanism, with the sulfur atom acting as the base, as has been proposed previously.[85]

**Figure 4-12.** The dual-site substrate-dependent mechanism involving both heterolytic and homolytic pathways.
2-methylquinoline seems to follow both mechanistic routes in parallel to produce 1,2,3,4-tetrahydro-2-methylquinoline (2m-\textsuperscript{1}THQ) at ‘Type A’ sites (70%) and 5,6,7,8-tetrahydro-2-methylquinoline (2m-\textsuperscript{5}THQ) (16%) at ‘Type B’ sites. The major product would be achieved through the heterolytic mechanism, similar to quinoline hydrogenation. However, due to the presence of a bulky methyl group next to the N- atom, adsorption of the carbocycle to the catalyst surface through $\pi$-$\pi$ interactions becomes competitive and, although at a lower rate, the homolytic mechanism operates in parallel to transfer hydrogen, and results in the formation of 2m-\textsuperscript{5}THQ. In the absence of methyl group (i.e. quinoline) no such interaction is observed, because there is a strong tendency for quinoline to engage in hydrogen bonding with the pyridinium group. In the case of indole, the lower basicity of the nitrogen atom also results in a lower tendency of the heterocycle to hydrogen-bond to the pyridinium sites and both mechanisms compete effectively for the substrate.

Based on these observations, we can conclude that we have successfully synthesized a catalyst (5 wt% Ru/py-CNTs) that undergoes heterolytic mechanism of hydrogen activation and ionic hydrogen transfer for the hydrogenation of heterocyclic rings, and/or homolytic hydrogen splitting and hydrogen atom transfer in the case of carbocyclic rings. When both are present in the same molecule, the basicity of the substrate and possible steric congestion around the nitrogen atoms determines the relative importance of each pathway. This is also supported by the high activity of 5 wt% Ru/py-CNTs towards arenes. As proposed by Fang et al, the hydrogenation of toluene occurs exclusively or predominately through homolytic hydrogen splitting mechanism at ‘Type B’ site on the catalyst (Ru/PVPy), whereas quinoline hydrogenation occurs at ‘Type A’ site that undergoes heterolytic splitting.\textsuperscript{[26]} The dual site nature
of 5 wt% Ru/py-CNTs is highly desirable, and leads to a wider scope of substrates, including N- and S-heteroaromatics as well as substituted arenes, for hydrogenation under mild conditions.

4.2.2.1.8. Dehydrogenation of 1,2,3,4-tetrahydroquinoline

Since we had already demonstrated that our Ru nanoparticle supported on carbon nanotubes catalysts are able to hydrogenate quinoline to 1,2,3,4-tetrahydroquinoline, the principle of microscopic reversibility dictates that the reverse dehydrogenation should be possible, as depicted in Scheme 4-6.

![Scheme 4-6. Hydrogenation-dehydrogenation of N-heteroaromatic compound by catalyst.](image-url)

To test our hypothesis, our two catalyst systems, 5 wt% Ru/Py-CNTs and 5 wt% Ru/AO-CNTs were tested for the dehydrogenation of 1,2,3,4-tetrahydroquinoline (1THQ) in the presence of 1-octadecene as the hydrogen acceptor at 150 °C, with [substrate]:[M] of 100, in a high-pressure vessel under inert conditions (Scheme 4-7). At the end of the reaction, the product composition was determined by GC-MS analysis for quinoline (only product observed). The TOF_{ave} was calculated based on moles of substrate converted per mole of ruthenium per hour. The results are collected in Table 4-5, below.

![Scheme 4-7. Dehydrogenation of 1,2,3,4-tetrahydroquinoline at 150 °C in the presence of 1-octadecene.](image-url)
Table 4-5. Dehydrogenation of 1,2,3,4-tetrahydroquinoline at 150 °C after 4h

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>% Conversion</th>
<th>TOF$_{\text{avge}}$ (h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 wt% Ru/Py-CNTs</td>
<td>17.5 ± 0.7</td>
<td>4.4 ± 0.2</td>
</tr>
<tr>
<td>2</td>
<td>5 wt% Ru/AO-CNTs</td>
<td>18 ± 1.8</td>
<td>4.5 ± 0.4</td>
</tr>
</tbody>
</table>

These results demonstrate that both ruthenium catalysts are capable of effectively dehydrogenating 1,2,3,4-tetrahydroquinoline (1THQ) to quinoline at mild conditions. As shown in Figure 4-13, the hydrogenation and dehydrogenation processes may be both explained by the same catalytic cycle. The black arrows moving clockwise indicate the hydrogenation pathway discussed in the preceding section, while the green arrows along the counterclockwise direction depict the dehydrogenation pathway. For the dehydrogenation reaction it is reasonable to propose that the 1THQ would first adsorb on a ‘Type A’ site (intermediate I) through weak hydrogen bonding, followed by a subsequent migration to ‘Type B’ (intermediate II), where two hydrogen atoms would be abstracted from the C3 and C4 carbon atoms, resulting in the formation of 1,2-dihydroquinoline, as the rate-determining step (rds). The 1,2-dihydroquinoline would then shift to the ‘Type A’ site, where the polar N- species would interact with active catalyst surface (intermediate III). The HN- on 1,2-dihydroquinoline molecule would hydrogen-bond to the basic nitrogen on the pyridine, while the hydrogen on the α-carbon would bind to the ruthenium nanoparticles to form a hydride, in an ionic ‘concerted transfer’. The proton on the pyridine functional groups and the hydride on the ruthenium metal would cleave off and release quinoline. Coupling and desorption of the hydride and the proton form a hydrogen molecule.
Our experimental data clearly indicate that the Ru/py-CNTs catalyst is much more active than the Ru/AO-CNTs catalyst in the hydrogenation of quinoline but both catalysts dehydrogenate THQ with essentially the same rate. Thus, the presence of the pyridine groups on the surface of the CNTs has a strongly activating effect in hydrogenation, in agreement with our mechanistic hypothesis, but no effect on the dehydrogenation of $^1$THQ. Since we believe both reactions follow the same catalytic cycle, this notable difference may be explained by different rate-determining steps for the two reactions. For the hydrogenation pathway, the rds must involve the pyridine group in the support; that is, the slow step of the cycle is either the heterolytic splitting of the hydrogen molecule, or the ionic hydrogen transfer from site A to the substrate. On the other hand, in dehydrogenation reaction over Ru/py-CNTs, the rds is probably the formation of 1,2-dihydroquinoline, which would take place by hydrogen abstraction from a C=C bond on ‘Type B’ sites. As this step takes place essentially on the metallic nanoparticle and does not involve any interaction of the substrate with the pyridine functional group on the surface, the Ru/py-CNTs catalyst would be expected to display a similar rate of dehydrogenation of $^1$THQ as the Ru/AO-CNTs catalyst, which is expected to be composed of ‘Type B’ sites, only, as observed in our experiments.
Figure 4-13. Possible dehydrogenation (green arrows) and hydrogenation (black arrows) mechanism of 1THQ and quinoline, respectively, over 5 wt% Ru/py-CNTs.

4.2.2.1.9 Computational studies on alternative hydrogenation/dehydrogenation substrate pairs

Besides finding new efficient dehydrogenation catalysts, another key issue is hydrogen storage in organic liquids to find the best substrate pairs that would allow the reaction cycle to be performed under reasonable conditions. We therefore decided to screen a large number of N-heterocyclic compounds, through a computational study of the thermodynamics of the dehydrogenation process for model systems. Using density functional theory (DFT) calculations, we evaluated the free energy change for the transfer of hydrogen from the heterocycle to a simple hydrogen acceptor like an alkene, as defined below in eq (1).

\[
\text{Saturated N-heterocycle} + \text{alkene} \quad \rightarrow \quad \text{Unsaturated N-heterocycle} + \text{alkane} \quad \Delta G \quad \text{eq(1)}
\]
The model compounds employed to be studied by the DFT calculations for the dehydrogenation for hydrogen storage purposes were selected on the basis of two structural features: 1) the number of nitrogen atoms on the heterocyclic ring as well as their relative positions in the ring, and 2) the number of carbon atoms present in the fused rings.

Since our results were based on the dehydrogenation of $^1$THQ with quinoline as the only product observed at 150 °C, all $\Delta G_{\text{150}^\circ C}$ values were normalized for $\Delta G_{\text{150}^\circ C}$ of $^1$THQ ($\Delta G_{\text{150}^\circ C}$ substrate/$\Delta G_{\text{150}^\circ C}$ $^1$THQ). For comparison, 9-ethylcarbazole, a known compound for its ability to release hydrogen at mild conditions (150-200 °C),[67] was also studied. The results of the calculations are summarized in Table 4-6. Based on our DFT calculations, 9-ethylcarbazole was found to be 1.2 times better than $^1$THQ (Table 4-6, entry 4) for the ease of dehydrogenation, although, as pointed out above, having the dehydrogenated product as a solid at room temperature is undesirable. We thus sought to discover other organic molecules that would be equal to, or better than dodecahydro-9-ethylcarbazole (normalized valued $\geq$1.2) for dehydrogenation at mild reaction conditions (Table 4-6, entry 3).

To test our hypothesis that increasing the number of nitrogen atoms and/or changing the number of carbon atoms in fused rings facilitates the dehydrogenation process, we changed the number and position of nitrogen atoms in a [6,6] fused ring. Starting with $^1$THQ (Table 4-6, entry 4) that has one nitrogen atom, we modeled compounds with two nitrogen atoms with the second nitrogen atom at the ortho, meta, or para positions, as shown in Figure 4-14. Based on our computational results, meta position (normalized 1.2) (Table 4-6, entry 10) had the most favorable effect, while the addition of N atom at the ortho and para positions did not have any additional impact on the $\Delta G_{\text{150}^\circ C}$, with the normalized values of 1.0 (Table 4-6, entries 7 and 13).
Figure 4-14. List of [6,6] fused rings with the number of nitrogen atoms at one, and two nitrogen at atoms at ortho, meta and para positions.

The effect of three nitrogen atoms on a [6,6] fused ring was also studied, as shown in Figure 4-15. Similar to the two nitrogen atom systems, the addition of nitrogen atom at the meta position (Table 4-6, entry 16) leads to a lower $\Delta G_{150^\circ C}$ than $^1$THQ (normalized 1.1), while no difference was observed at the para position (normalized 1.0) (Table 4-6, entry 19). However, overall, increasing the number of nitrogen atoms from two to three did not decrease the $\Delta G_{150^\circ C}$ significantly.

Figure 4-15. List of [6,6] fused rings with the number of nitrogen atoms at ortho, meta and para positions.

Five membered rings (see Figure 4-16) with different number of nitrogens were also studied (Table 4-6, entries 22–25). A much more pronounced effect of nitrogen atom(s) was observed in these systems; an increase in the number of nitrogen atoms from one to three
lowered the Gibbs free energy by half (normalized 1.7) (Table 4-6, entry 25). It is interesting to note that similar results have been reported in a study by Clot et al for acceptor-free dehydrogenation of five- and six-member ring systems.\[86\]

\begin{center}
\begin{tabular}{c}
\includegraphics[width=0.5\textwidth]{figure16.png}
\end{tabular}
\end{center}

**Figure 4-16.** List of five membered rings with the number of nitrogen atoms ranging from 1–3.

Inspired by the results obtained for the five membered systems in the previous study, we expanded our calculations to [6,5] fused rings (e.g. indole) (Table 4-6, entries 26-36), as shown in Figure 4-17. The addition of nitrogen atom in the N2 and N3 positions had a significant influence on the $\Delta G_{150^\circ C}$, with the normalized value of 1.7 for each compound. The addition of third nitrogen, however, had the best results of all systems studied, with the normalized value of 2.1 (Table 4-6, entry 34) among all the systems studied.

\begin{center}
\begin{tabular}{c}
\includegraphics[width=0.5\textwidth]{figure17.png}
\end{tabular}
\end{center}

**Figure 4-17.** List of [6,5] fused rings with the number of nitrogen atoms ranging from 1–3.
Table 4-6. Thermodynamic data ($\Delta G_{150\, ^{\circ}C}$) per H$_2$ molecule released as obtained from B3LYP/cc-pVDZ calculations.

<table>
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<th>Entry</th>
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<th>Normalized for $^1$THQ</th>
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4.3. Conclusions

In this work, we had set out to synthesize new nanostructured catalytic materials composed of basic functionalities adjacent to active metal sites on high surface area, low porosity carbon nanotubes supports that can promote heterolytic hydrogen splitting to enhance catalytic activity and prevent poisoning. We have successfully synthesized and characterized 5 wt% Ru/py-CNTs using TEM, XPS, and XRD. These characterization techniques confirm that our new material is composed of metallic Ru nanoparticles supported on pyridine-functionalized carbon nanotubes. The catalytic tests of 5 wt % Ru/py-CNTs for hydrogenation of a variety of substrates with the main focus on N- and S-heteroaromatic, and methyl substituted arene compounds representative
of components of fossil fuels indicate that catalyst is extremely efficient and selective in hydrogenating five membered (pyrrole), six membered (pyridine, toluene, xylene, and mesitylene) and fused rings (indole, quinolines, and benzothiophene).

Moreover, herein we were able to validate our central hypothesis that the presence of basic functionalities adjacent to active metal sites enhances the catalytic activity, particularly for polar N- and possibly S-heteroaromatic compounds. The activity of carbon nanotubes supported ruthenium catalyst (Ru/AO-CNTs) was drastically improved by covalently functionalizing the carbon nanotubes with pyridine rings prior to the ruthenium metal deposition (5 wt % Ru/py-CNTs).

While, with an average TOF$_{\text{init}}$ of 3600 ± 700 h$^{-1}$, Ru/AO-CNTs exclusively hydrogenates quinoline to 1,2,3,4-tetrahydroquinoline, the Ru/py-CNTs exhibits much higher activity towards quinoline with an average TOF$_{\text{init}}$ of 6000 ± 800 h$^{-1}$. The summary of average TOF$_{\text{init}}$ for the hydrogenation of quinoline by Pd/MgO, Ru/AO-CNTs, and Ru/py-CNTs, which illustrates the continuous progress achieved during the course of this dissertation, is depicted in Figure 4-18.
Figure 4-18. TOF$_{\text{init}}$ for the hydrogenation of quinoline by 1 wt% Pd/MgO, 5 wt% Ru/AO-CNTs, and 5 wt% Ru/py-CNTs at 150°C and 40 atm H$_2$.

Moreover, as mentioned earlier in this chapter, our newest catalyst, Ru/py-CNTs, is considerably more active than any other catalyst reported in the literature for the reactions described.

With the positive results in hydrogenation of N-heteroaromatics using 5 wt% Ru/py-CNTs and 5 wt% Ru/AO-CNTs, we also explored the dehydrogenation capabilities of these catalysts for the study of N-heteroaromatics in relevance to hydrogen storage applications using organic liquids. Dehydrogenation of 1,2,3,4-tetrahydroquinoline (1THQ) yielded quinoline with TOF$_{\text{avge}}$ ranging from 4.4-4.5 h$^{-1}$, indicating that the hydrogenation/dehydrogenation cycle promoted by these catalysts (Figure 4-19) might be of interest for hydrogen storage purposes.
Using $^1$THQ as a baseline, we expanded our search for the best pairs of organic liquids for hydrogen storage purposes by performing DFT calculations on 36 model systems. Overall, most compounds studied were exothermic, with slight variation in energy. The summary of the results is depicted in Figure 4-20, below. Based on these computational results, fused [6,5] membered rings with three nitrogen atoms, 1H-benzo[d][1,2,3]triazole (Table 4-2, entry 35) is thermodynamically the best organic compound for dehydrogenation. However, this compound is a solid at room temperature, and therefore, it is not suitable as a hydrogen storage material for transportation purposes. With the normalized value of 1.7, the second best compound based on our results, is 1,2,3-triazolidine (Table 4-6, entry 34). This compound is also liquid at room temperature in both hydrogenated and dehydrogenated forms, and has a storage capacity of 5.5 wt% H$_2$, making it optimal for liquid organic hydrogen storage applications.
Figure 4-20. Comparison of the highest normalized $\Delta G_{150 \, ^\circ C}$ values for each ring system.

A possible disadvantage associated with these compounds is that they are not commercially available. The synthesis and catalysis study of these molecules falls outside the scope of this dissertation, but based on the calculated thermodynamic parameters, they are worthy of further study.

4.4. Experimental

4.4.1. Materials

RuCl$_3$.3H$_2$O (Pressure Chemicals, Inc.) was used as purchased. Solvents (analytical grade, Sigma-Aldrich) were purified using a PureSolv purification unit from Innovative Technology, Inc. and further deoxygenated with a nitrogen flow prior to use. Substrates and other reagents (Sigma-Aldrich) were purified by appropriate methods prior to use as necessary. Multiwalled carbon nanotubes (Sigma-Aldrich) were functionalized using known methods.$^{[71]}$
4.4.2. Catalyst preparation and characterization

4.4.2.1. Synthesis of pyridine functionalized carbon nanotubes (py-CNTs)

Multiwalled carbon nanotubes were purified at 400 °C under a N₂ flow, followed by 6 M HCl treatment overnight. The purified MWNTs were filtered over nylon membrane (0.2 μm, Whatman) and washed with ultra high purity water until pH neutral. The purified MWNTs were then annealed at 900 °C under vacuum for four hours. To functionalize the purified nanotubes with pyridine, a cooled solution of NaNO₂ (98.0 g, 1.4 mol) in 140 cm³ water was added dropwise to 4-aminopyrdine (131.6 g, 1.3 mol) in 1000 cm³ 4 M HCl at 0 °C. After the slow addition was complete, the solution mixture was further stirred for ~ 1 h. To the cooled solution, purified MWNTs (2.0 g) in 50 cm³ dimethylformamide (DMF) were added dropwise at 0 °C and stirred for 4 h. The reaction mixture was further stirred for 72 h at room temperature. The functionalized carbon nanotubes were then filtered through nylon membrane (0.2 μm, Whatman) and dispersed in 2 M HCl (100 cm³) followed by neutralization with water. The CNTs were then stirred overnight in 100 cm³ sodium hydroxide solution (2 M) to deprotonate the pyridinium salt. The pyridine-functionalized carbon nanotubes (py-CNTs) were then washed with deionized water until pH neutral, followed by THF (2 × 30 cm³), acetone (2 × 30 cm³), and ethanol (2 × 30 cm³). The carbon material was then dried overnight under vacuum.

4.4.2.2. Synthesis of Ru/Py-CNTs

To prepare the 5 wt% ruthenium catalyst, the support (pyridine functionalized carbon nanotubes) [71] (1.0 g) was placed in a 3-neck round bottom flask under nitrogen. Dry deoxygenated methanol (10 cm³) was added and the mixture was stirred. Two pressure-equalizing dropping funnels were attached to the flask, one containing RuCl₃.3H₂O (0.130 g; 0.05 g Ru) in dry deoxygenated methanol (10 cm³) and the second containing NaBH₄ (0.190 g)
in the same solvent (20 cm$^3$). Approximately 10 cm$^3$ of the borohydride solution was added quickly to the flask and the mixture was stirred for a few minutes. Subsequently, both the RuCl$_3$.3H$_2$O and the remaining NaBH$_4$ solutions were added simultaneously to the flask at the rate of about one drop per second. After the addition was complete, the dark mixture was stirred overnight under nitrogen at room temperature. The product was filtered under nitrogen, washed three times with methanol (10 cm$^3$), and dried under vacuum at room temperature overnight.

4.4.2.3. TEM studies

Transmission electron microscopy analysis was conducted using JEOL-2010 high-resolution microscope, operating at a voltage of 200 kV and providing point-to-point resolutions of 0.19 nm. Samples for analysis were prepared by placing a drop of a suspension of the catalyst in hexane on a copper grid and allowing it to air-dry. Images were captured using an AMT camera system.

4.4.2.4. XPS measurements

The x-ray photoelectron spectroscopy was performed using an Omicron XPS spectrometer equipped with a multichannel hemisphere analyzer and a dual Al/Mg X-ray source using Al K$_\alpha$ excitation (1486.6 eV). The powdered sample was mounted on studs using a double-sided adhesive tape in air. The data analysis was performed by deconvoluting the XPS peaks by curve fitting using XPSPEAKS 4.1, applying Shirley background subtraction and Lorentzian-Gaussian functions (20% L, 80% G). The charging effect was corrected based on the literature value of 284.5 eV for the C 1s peak in py-CNTs.$^{[71]}$
4.4.2.5. XRD measurements

Powder X-ray diffraction (XRD) patterns were obtained on a Phillips X’PERT MPD diffractometer using monochromatic Cu-Kα radiation at 45 kV and 40 mA and 2θ scanning from 0° to 80°. Samples were ground in a mortar prior to analysis in air at room temperature.

4.4.3. Catalytic tests

4.4.3.1. Hydrogenation of N-heteroaromatics

Hydrogenation of N-heteroaromatic substrates was carried out in a glass-lined 5000 Parr multireactor (75 cm³) equipped with a magnetic stirrer and a thermocouple, and coupled to a 4871 controller. Typically the reactor was loaded with the catalyst (50 mg; Ru = 0.025 mmol) and the desired amount of substrate (25 mmol or 2.5 mmol). The reaction mixture was deoxygenated by flushing with H₂ (20 atm) three times. The reactor was pressurized with H₂ at room temperature to 33 atm and then heated while stirring at 50 rpm until the temperature reached 150 °C. The stirring rate was increased to 650 rpm at that point, which was taken as the zero time for the reaction. The progress of the reaction was followed by monitoring the H₂ uptake. At the end of the run, a sample of the final mixture was analyzed by GC-MS using a Varian 3900 gas chromatograph fitted with a SP2330 capillary column and a Saturn 2100T mass detector. TOF_{init} values were calculated from the slope of the linear part of P vs. t plots. Average TOF values were obtained from at least three experiments.

4.4.3.2. Recycling experiments of 5 wt% Ru/py-CNTs

For each cycle, the hydrogenation reactions were performed in a glass-lined 5000 Parr multireactor, as described above. At the end of each cycle, the catalyst was isolated by adding hexane (~30 cm³) and stirring the reaction mixture for ~ 1 min. The solid was then allowed to
settle at the bottom of the liner and the liquid was pipetted out and filtered over a nylon member (0.2 μm, Whatman). The washing was carried out (~3-6 times) until the liquid became colorless, and the solid became well dispersed and began to move freely in hexane. The isolated catalyst, from the liner and the nylon membrane filter, was combined and dried overnight prior to the next hydrogenation cycle.

4.4.3.3. Dehydrogenation of N-heteroaromatics

A typical dehydrogenation of 1THQ was carried out in a glass-lined 5000 Parr multireactor (75 cm³) equipped with a magnetic stirrer and a thermocouple, and coupled to a 4871 controller. The reactor was loaded with the catalyst (50 mg; Ru = 0.025mmol) and the desired amount of substrate (0.0025 mol). The reactor was sealed under inert conditions and the reaction mixture was heated while stirring at 50 rpm until the temperature reached 150 °C. Stirring rate was increasing to 650 rpm at that point, which was taken as the zero time for the reaction. At the end of the run, a sample of the final mixture was analyzed by GC-MS using a Varian 3900 gas chromatograph fitted with a SP2330 capillary column and a Saturn 2100T mass detector. TOF_{ave} is defined as moles of substrate converted per mol of Ru per hour. Average TOF values were obtained from at least two experiments; the dispersion observed between individual measurements was less than 10%.

4.4.4. Computational methods

All structures were fully optimized using B3LYP\(^ {[87]}\) density functional method as implemented in the Gaussian09 suite of quantum chemical programs.\(^ {[88]}\) All structures were characterized as true minima on the potential energy surface by calculating normal models of vibrations. A correlation consistent basis set of double-\(\zeta\) quality is used for all the calculation.\(^ {[89]}\) All
thermochemistry data were computed at the room temperature and atmospheric pressure, and further extrapolated to 150 °C.
Bibliography


